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Hydrogen Production by Catalytic Steam Reforming of Urea

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ABSTRACT – This work reports for the first time experiments of hydrogen production by steam reforming of urea. Urea could fulfil present targets for hydrogen storage in transport applications, with a higher gravimetric H₂ content available when it is reformed to H₂ and CO₂ using steam. It is a non-toxic, non-flammable compound in pure form that is stable at room temperature and atmospheric pressure. It has a pre-existing manufacturing infrastructure, being a cheap and widely available market commodity with well-established methods for production, storage and distribution. Renewable production routes of urea are identified. Thermodynamic equilibrium calculations identified the feasibility of urea steam reforming for H₂ production. In order to ensure a significant catalyst activity, experiments using a continuous flow packed-bed reactor were conducted at 600 °C for steam to carbon ratios between 4 and 7 at atmospheric pressure using a nickel-based catalyst. Experimental results agreed well with thermodynamic calculations, with a dry syngas containing H₂, CO₂, N₂, little CO, and negligible amounts of CH₄ and no NH₃ or other hydrocarbons, resulting in the expected H₂ yield per mole of urea feed approaching 3. Complete conversion of urea was predicted and observed experimentally to within 5% for steam to carbon ratios from 5 to 7. Experimental steam conversion values were between 10-15%. Unconverted steam leaving the reactor retained any ammonia produced thus enabling it to be easily removed from the syngas via condensers.

Keywords: hydrogen, urea, nickel, steam reforming.

I. INTRODUCTION

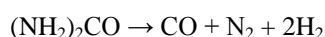
A number of compounds have been evaluated as potential hydrogen carriers that ideally would possess simple, rapid and inexpensive dissociation mechanisms providing hydrogen and have the ability to be either recharged or release only environmentally benign by-products.

The ideal engineering solution for hydrogen extraction would be to split water into its elements because of its abundance; but its thermodynamic stability makes water dissociation difficult to achieve in practice. Current economic large-scale production of hydrogen is predominantly from hydrocarbons (particularly methane) and water via steam reforming (R1), which is strongly endothermic. This reaction is brought to equilibrium at high temperature over a nickel catalyst [1]-[3] and is followed by the mildly exothermic water gas shift reaction ‘WGSR’, (R2) that provides the full hydrogen potential of the overall steam reforming reaction [4].

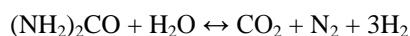


Industrial steam reforming is a mature technology being operated since the 1930s. Today natural gas is usually the preferred feedstock. Alternative sustainable biofeedstocks such as sunflower oil, and glycerol are being successfully explored in the laboratory [1], [2]. Urea (NH₂)₂CO can be

seen as potentially yielding two moles of H₂ via thermal decomposition, as illustrated in reaction R3, and the involvement of steam provides a further mole of H₂ (via the complete reaction R2), as in reaction R4, that shows the stoichiometric steam to carbon ratio (S:C) is 1:1.



$$\Delta H^\circ_{298} = + 121.4 \text{ kJ mol}^{-1} \quad (\text{R3})$$



$$\Delta H^\circ_{298} = + 80.4 \text{ kJ mol}^{-1} \quad (\text{R4})$$

The maximum molar yield of H₂ per mol of urea is therefore 3. As a H₂ carrier, urea has a gravimetric hydrogen content of 6.71 wt%, fulfilling present DOE targets for hydrogen storage in transport applications [5]. With the additional molecule of H₂ available when water is included from steam reforming, the value is 7.95 wt% of stoichiometric urea-water solution, or 10.07 wt% of urea. Urea steam reforming has not previously been reported as a hydrogen energy vector although it has been shown that hydrogen can be produced from urea by electrolysis, using aqueous solutions similar to urine [6]. Urea is a widely available commodity with commercial production plants operating the well-established reaction of ammonia (NH₃) with carbon dioxide (CO₂) via ammonium carbamate at elevated temperature and pressure.

The global demand for urea is increasing, with an expected increase of 30.2 Mt from 150Mt in 2008 to 180Mt in 2012 [7]. Its main use is as a slow-release nitrogen fertiliser, and increasingly to control nitrogen oxides emissions into the environment via selective catalytic reduction (SCR) [8]-[10]. Though commercial production of urea is from natural gas via ammonia, it has the potential of being sourced sustainably, and means of producing urea from renewable sources, such as urine and bacteria will be explored in a forthcoming publication.

Urea has several advantages over presently proposed hydrogen carrier compounds. It is a non-flammable, non-toxic, stable, odourless, crystalline solid at room temperature enabling easy storage and transport with only dry containment being required. This is an immediate advantage over other hydrogen carriers such as ammonia (NH_3), which is a toxic gas [11]. Moreover, urea is biodegradable and classified as having “no indication of concern for human health or the environment” [12]. It is excreted by mammals, fish, amphibians, zooplankton and bacteria [13]-[16], [17]. Consequently it is naturally present in balanced water ecosystems [13]-[16]. Urea’s content in urine is approximately 2 wt%, representing a molar ratio of water to carbon of 159:1. It also exists in plants, where it is believed to be a nitrogen store [18].

Recent work has been focussed on urea in aqueous solution due to its use in SCR NO_x emissions control systems. This application commonly involves a eutectic mixture at -11°C and 32.5 wt% urea.

We have confirmed the viability of urea steam reforming for hydrogen production, and the present study gives details of thermodynamic calculations and the results of our laboratory experiments.

II. EXPERIMENTAL

A. Thermodynamic Calculations

Thermodynamic calculations were undertaken to ascertain the feasibility of urea steam reforming, to identify optimum high conversion conditions, and to indicate possible major by-products. The computation software used was EQUIL [19], a FORTRAN programme part of the CHEMKIN software suite, which included CH_4 , CO , CO_2 , O_2 , H_2O , H_2 , N_2 , NH_2 , NH_3 , $\text{CH}_4\text{N}_2\text{O}$ (urea), HNCO and HCN as potential equilibrium products. The calculations were performed with urea solutions of S:C = 1, 2, 3, 4, 5, 6 and 7 using a N_2 mol fraction of 0.631, a value close to those used in the experiments (0.611-0.631), and over the temperature range 300 K to 1280 K. Output values were tabulated at 10 K intervals.

B. Experimental Methods and Materials

Urea (>99.5%) was purchased from Fisher Scientific, and de-ionized water was used in all the experiments. The catalyst contained 18 wt% NiO on a proprietary Al_2O_3 support that was provided by Johnson Matthey as pellets 13.8 mm diameter and 18.4 mm long, that were crushed and sieved to give a 0.66 - 1.70 mm size range cut for the steam reforming experiments. Each experiment used undi-

luted 20 grams of catalyst occupying a volume of 10.5 cm^3 within the reactor tube, supported on a stainless steel circular mesh screen. The surface area of the catalyst and other properties were reported previously [1]. A schematic diagram of the drop-feed continuous downflow packed-bed quartz reactor and the ancillary equipment is shown in Figure 1.

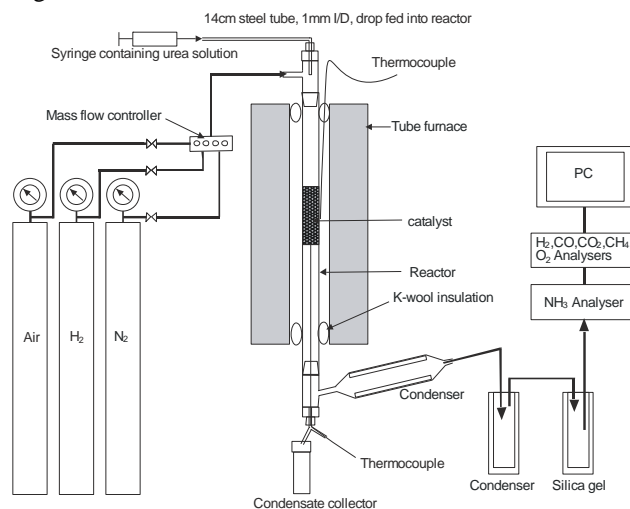


Figure 1 – Schematic Diagram of the Experimental Setup.

The reactor tube was 70 cm long with an internal diameter of 12 mm, connected at the bottom to a glass outlet assembly and condenser, and at the top to a glass inlet section. The reactor was heated by a tube furnace with a programmable temperature controller using a thermocouple measurement attached on the internal wall of the furnace. K-wool insulation was packed into the 16 mm space between reactor tube and furnace walls to a depth of 4cm at the outer edges. Two K-type thermocouples (one embedded in the catalyst, and one the reactor wall adjacent to the middle of the catalyst bed) were used to measure the reactor bed temperature, and in the latter case, also control it. Inlet N_2 and H_2 gases from BOC cylinders of >99.99% purity were regulated by MKS mass flow controllers. Steel tubing (14 cm long, 1 mm internal diameter) connected a syringe pump to the inlet assembly then through a 90° bend via Swagelok connector to a 2mm I/D steel tube. This tube’s outlet was situated centrally 2cm above the reactor tube top and horizontally adjacent to the gas inlet. N_2 carrier gas was used in all of the experiments with a flow of $300\text{ cm}^3\text{ min}^{-1}$ (STP) and the system was at atmospheric pressure. Prior to each steam reforming experiment, the catalyst was reduced at 500°C by a flow of $30\text{ cm}^3\text{ min}^{-1}$ (STP) of H_2 in $400\text{ cm}^3\text{ min}^{-1}$ (STP) of N_2 , and after 1 hour the reactor was purged for at least ten minutes with the same flow of N_2 . Aqueous urea was then introduced at a rate of 10 ml/h (20°C) into the reactor via a micro-syringe pump (New Era Pump Systems). The reactor gaseous effluent was passed through two oil-cooled condensers and a silica gel trap to remove moisture before analysis. Condensate was collected in a glass flask at the base of the outlet assembly for analysis of its ammonia content.

Steam reforming was performed on urea solutions of S:C = 4, 5, 6 and 7:1 molar ratio at a set reactor temperature of 600°C. Fresh catalyst was used for each S:C ratio experiment. Following each steam reforming step, the system was purged with N₂ at the same flow rate and temperature to remove any residual gases. Then, an air feed of 1000 cm³ min⁻¹ (STP) maximum was applied at 700°C. This airflow step allowed for an assessment of possible coke build-up on the catalyst surface by observation of the resulting CO₂ or CO detection.

C. Product Analysis

The dry product gases were measured online with a series of (non sample-destructive) ABB Advance Optima Analysers comprising a Uras 14 non-dispersive infrared absorption module for CO, CO₂ and CH₄ analysis, a Caldos 15 thermal conductivity analysis module for H₂, and a Limas 11 ultraviolet absorption module for NH₃ analysis. Product concentration values were obtained every five seconds. During the air feed stage, oxygen was analysed at the end of the line using a Magnos 106 paramagnetic susceptibility module also by ABB Advance Optima.

At cessation of the steam reforming step, condensate was collected immediately and stored in glass vials and in dark refrigerated conditions. This was then analysed using a Dionex DX-100 Ion Chromatograph at room temperature, with 0.02 mols methane sulphonic acid as eluent and Dionex polymeric packing (IONPAC CS12A), on a column 4 mm × 250 mm. Raw samples were diluted with deionised water to fit within the detection range of the analytical technique and were analysed at room temperature.

Off-line gas chromatography was carried out by collecting product gas samples in a Tedlar bag at the end of the on-line sampling period. For hydrocarbons from C₁ to C₄, a Varian 3380 gas chromatograph with a flame ionisation detector (GC/FID) was used with N₂ as a carrier gas and with a 2 mm × 2 m column packed with 80-100 mesh Haysep material. H₂, CO, O₂, N₂ and CO₂ were analysed by a Varian 3380 GC with two packed 2 mm × 2 m columns and with two thermal conductivity detectors (GC/TCD). H₂, CO, O₂ and N₂ were analysed on a column packed with 60-80 molecular mesh sieve, with argon as carrier gas. CO₂ was analysed on a column packed with 80-100 mesh Haysep.

D. Data Analysis

Conversions and products selectivity were calculated with a mass and elemental balance spreadsheet using reactor exit concentrations of H₂, CO, CO₂, CH₄ and NH₃ (gas and liquid). The possible presence of volatile hydrocarbons higher than CH₄ was eliminated by the lack of detected products other than CH₄ from the off-line GC/FID analyses. The unmeasured product N₂ mol fraction was calculated by difference from 1 of the sum of the measured gases, and H₂O was predicted via the hydrogen balance in the spreadsheet calculation. Urea conversion was calculated based on the carbon-containing product concentrations

and the urea feed rate.

III. RESULTS AND DISCUSSION

The thermodynamic calculations predicted complete urea conversion for all feed ratios considered at temperatures between 30 and 1000°C, though positive values for calculated steam conversion did not occur below 300°C (not shown). Figure 2 shows the H₂ yield predicted by the thermodynamic calculations (in mol of H₂/mol of urea in feed). It exhibited a maximum for a given steam to carbon ratio which approached the ideal value of 3 (corresponding to the complete conversion of urea and steam to H₂, CO₂ and N₂) as the steam to carbon ratio increased.

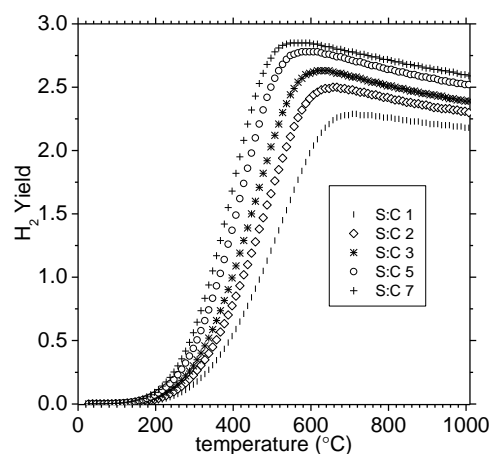


Figure 2. Calculated equilibrium hydrogen yield (mol H₂ produced / mol urea in the feed) as a function of temperature for steam to carbon ratios from 1 to 7 and with a fixed N₂ mol fraction of 0.631.

Indeed, the H₂ yield for S:C=7 peaked at 2.85 mol H₂/mol urea in the temperature range 547-597°C, compared to 2.29 mol H₂/mol urea at 707-717°C for S:C=1. Whereas the relatively steep rise of H₂ yield at low (< 400-600°C) but increasing temperature for a given S:C ratio was caused by the medium endothermicity of the steam reforming of urea and of its thermal decomposition products (specifically CH₄). The decrease in H₂ yield at post peak temperatures was caused by the mild exothermicity of R2 and thus by the reverse water gas shift becoming more favourable. The calculated steam conversions (see Table 2) indicated that the optimum temperatures for urea steam reforming for S:C of 3 and above were within a range where the water gas shift reaction still dominates over its reverse. Consequently, and unlike methane steam reforming, there would be no need for separate high temperature and low temperature WGS reactors, as the unreacted CO at these temperatures would be negligible. In addition, urea steam reforming, like glycerol [2], would be a good candidate for in-situ CO₂ capture (sorption enhanced steam reforming), which operates best at temperatures at or below 600°C where the CO₂ production from the WGS is still significant. In-situ CO₂ capture as a means of pre-combustion or post-combustion fuel decarbonisation is a process that is gathering fast-growing interest in gasification and power generation applications. It is expensive to raise steam, therefore the lowest S:C ratio

while operating with super-stoichiometric steam, used in combination with the lowest temperature required for the catalyst to display steam reforming activity offer the optimum experimental conditions. Therefore the temperature of 600°C was chosen with the range of steam to carbon ratios being determined by the solubility of urea in water at ambient temperature.

Experimental dry product gas concentrations as a function of time, typical of the set of experiments conducted at S:C from 4 to 7, are displayed in Figure 3 for S:C of 7 along with their respective equilibrium calculated values (shown as dotted lines). Mean averages of H₂ product concentrations at steady state for S:C of 4, 5, and 6 were 17.7%, 17.6%, and 16.1% respectively. Ratios of major product concentrations for all experiments are shown in Table 2. As experimental products were diluted by nitrogen carrier gas and product nitrogen, the values shown in Figure 3 are displayed as mole % of the syngas with the balance being N₂.

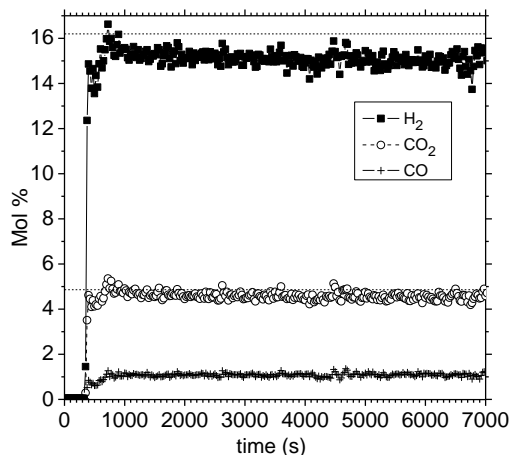


Figure 3. Dry product gas concentrations for steam to carbon ratio of 7, shown as scatterpoints as a function of time, using 20% of datapoints for clarity. Also shown are calculated equilibrium data displayed as dotted lines for each species. Methane (<0.03%) and Ammonia (0%) at steady state omitted.

It is worth noting that the mol % of H₂ in the syngas, and as shown for S:C 7 in Figure 3 (15.2%) are not representative of the syngas H₂ content that would be achieved in an industrial process. The N₂ dilution in the present study was used only for elemental balances purposes and to achieve the minimum flow required by our online analysers. In a practical setting, CO₂ may be used as a carrier gas in order to ease the liquid feed, and then removed by a CO₂-sorbent either in the reformer or downstream, prior to feeding a fuel cell. For a polymer electrolyte membrane fuel cell (PEMFC) the dilution affects of N₂ with the H₂ feed have been shown to have a beneficial effect in stabilising power outputs when demand fluctuates [20].

Table 2 lists the experimental urea and steam conversion fraction derived from the elemental balances, H₂ yield per mol of urea in the feed, and the products distribution at steady-state, compared to their equilibrium calculated counterparts for S:C from 4 to 7. It can be seen that the closeness of the experimental outputs with the calculations proved that the conditions were close to equilibrium. These were based on steady state conditions over 1.5 hours indicating good process stability and no degradation of catalyst activity. This also suggests that coking of the catalyst was not significant. Further support for this assertion was, aside from the fuel conversions being close to 1, by the absence of CO₂ and CO detected during the oxidation conditions of the final air feed step (not shown). The carbon products selectivity values were also close to equilibrium and beneficially, in terms of its high greenhouse gas potential, CH₄ was not produced in significant amounts at any time. Results of the off-line GC analysis revealed that the product gas contained no other higher hydrocarbon species. Analysis of NH₃ was considered important due to its deleterious effect to PEMFCs [21], [22]. It was found that during steady state, gaseous NH₃ was not present even

Table 2. Mean experimental and calculated equilibrium reactant conversions and products distribution at 600°C. H₂ Yield values are calculated from mol H₂ produced/mol urea in the feed

S:C		H ₂ Yield	x_{urea}	x_{H_2O}	Selectivity C-products %			H ₂ :CO ₂	H ₂ :CO
					CO ₂	CO	CH ₄		
4	Experimental	2.22	0.90	0.15	73.6	25.5	0.01	3.4:1	10:1
	Equilibrium	2.72	1.00	0.19	75.5	23.4	1.14	3.6:1	12:1
5	Experimental	2.52	0.95	0.15	76.88	22.60	0.01	3.5:1	12:1
	Equilibrium	2.78	1.00	0.16	79.9	19.5	0.59	3.5:1	14:1
6	Experimental	2.51	0.94	0.13	74.9	24.3	0.01	3.5:1	11:1
	Equilibrium	2.82	1.00	0.14	83.0	16.7	0.34	3.4:1	17:1
7	Experimental	2.60	0.99	0.10	80.7	19.1	<0.01	3.3:1	14:1
	Equilibrium	2.85	1.00	0.12	84.8	15.1	0.10	3.3:1	20:1

at < 10ppm level and that all ammonia was retained in the condensate. Table 2 shows values of ammonia concentration in the condensate. Diluted samples were pH tested and seen to have a neutral pH of 7. The acidity of the eluent was not tested but was expected to be only mildly acidic due to its low concentration. Therefore it was expected that eluted samples would have had a pH of 6 or 7 as they passed through the analytical column. Based on this assumption and from previous studies of the dependency of ammonia concentrations in solution to pH and temperature [23], it is expected that the results provided in Table 2 are minimum values correct to + 0.02-0.5% relative uncertainty.

Table 2 – Molar NH₃ concentration in the condensate following steam reforming in gravimetric parts per million (ppm)

S:C	7	6	5	4
NH ₃ (ppm)	6926	14396	14559	26557

It can be seen from Table 2 that NH₃ was produced with urea steam reforming and increased with urea content in the feed solution as would be expected. The increase in ammonia with decreasing reactor temperature is likely due to lower catalytic activity. Nickel catalysts have shown activity for splitting NH₃, with conversion increased with higher temperature [11]. In terms of process design it is advantageous that ammonia is trapped and collected in the condensate since this would ease the process of direct syngas supply to PEMFCs.

In terms of stability, highest steam and urea conversion, and closeness to predicted equilibrium values, S:C 7 yielded the best results. This concentration approximated to a urea wt% of the eutectic mixture (32.5wt%) that is used in SCR of NO_x, thus offering the possibility of dual application with integrated hydrogen supplied fuel cell/combustion technology.

IV. CONCLUSIONS

Thermodynamic calculations showed there is an optimum temperature for the steam reforming of urea for H₂ production that is caused by the juxtaposition of the relatively mild endothermic steam reforming reaction with the weak exothermicity of the water gas shift reaction. Combining this theoretical temperature range with the need to minimise the cost of raising steam and operate with an activated catalyst resulted in an optimum temperature for hydrogen production from steam reforming of urea at around 600 °C. These points were confirmed experimentally using a Ni catalyst at steam to carbon ratios from 4 to 7. For all feed ratios, experimental conversion of urea was 90-99% complete and values of water conversion of 10-15% were observed proving that steam reforming was close to predicted thermodynamic equilibrium. Hydrogen was the major experimental dry gas product, with carbon dioxide in a ratio of H₂:CO₂ from 3.3:1 to 3.5:1. CO was detected as a minor syngas product present in the range of H₂:CO from 10:1 to 14:1. CH₄ was not detected in significant amounts and there were no higher hydrocarbons created. Urea is a naturally occurring substance and these low

values of greenhouse gas products (particularly methane) make it a highly attractive future hydrogen carrier for fuel cells if the huge sustainable resource of urea could be subjected to significant research focus and employed. Urea has the added advantage of being stable and non-toxic, with a molecular hydrogen mass content that meets present target values.

Experimental H₂ yields based on mole of urea in the feed were close to the ideal values of 3 predicted by complete urea conversion to H₂, CO₂, and N₂. Carbon deposition was not observed visibly or detected analytically. The potential for applying sorption enhancement by using a CO₂ sorbent in the reactor is high, this would result in a H₂/N₂ output flow.

NH₃ was produced in low levels during steam reforming, present in higher quantity with higher feed urea concentration. All NH₃ was retained within the unconverted steam leaving the reactor and therefore being contained by condensers and ultimately removed from the syngas. This simple NH₃-trapping mechanism could be highly advantageous in terms of potential direct supply to PEM fuel cells which are intolerant to NH₃.

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He is a second year PhD student studying hydrogen production by steam reforming and has interests in sustainability and renewable energy technologies.

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Gavin L. Rickett – Born in Leeds, England, 1980. PhD in Fuel and Energy, 2007 and BSc (Hons) in Fuel & Combustion Science, The University of Leeds, England, 2003.

He is a post-doctoral research assistant with expertise in noble metal supported catalytic combustion and hydrogen production from advanced steam reforming processes.

Dr Gavin L. Rickett

Valerie Dupont – Born in Lille, France, 1967. PhD in Fuel and Energy, The University of Leeds, UK, 1994, Dipl. Ingenieur INSA-Lyon (Energy Eng.), France, 1989.

Her publications focus on the mechanisms of nitrogen oxides formation in flames, on noble metal supported catalytic combustion, and more recently, on advanced steam reforming processes for the production of high purity H₂ from sustainable feedstocks.

Dr Valerie Dupont, member of IChemE catalysis group and The Combustion Institute (British Section).

Martyn V. Twigg – Martyn Twigg is the Chief Scientist of Johnson Matthey PLC and previously Technical Director for the Environmental Catalysts and Technologies Division.

Following work at the University of Toronto, Canada, and a fellowship at the University of Cambridge, U.K., he joined ICI where he aided the development and production of heterogeneous catalysts used in the production of hydrogen, ammonia and methanol. He has authored or co-authored many research papers, written numerous chapters in encyclopedic works, and edited and contributed to several books. He edits a book series on fundamental and applied catalysis.

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