

Combining Residual Gas Analysis and Differential Scanning Calorimetry to Develop Catalysts for Low Energy N₂O Microthrusters

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Abstract

8%CuO_x/ZnO_y and 8%Co,4%CuO_x/ZnO_y are shown by residual gas analysis (RGA) and differential scanning calorimetry (DSC) to be active in sustained N₂O decomposition above 773K. Transient experiments on 8%CuO_x/ZnO_y at 473K suggest that UV irradiation enhanced this reaction (and the subsequent desorption of O₂) and moreover this activity was retained even after the irradiation of the catalyst is terminated. This may be important in the propulsion of small satellites with a low power requirement, but new materials technology will be required.

1. Introduction

(a) Catalytic Microthrusters in Satellites

There is a trend towards decreasing the mass, dimension, complexity and cost of space systems [1]. An aspect of this is the increasing potential of smaller satellites with more effective propulsion to form constellations, to change or maintain orbits and to compensate for atmospheric drag. This has traditionally employed cold gases (e.g. N_{2(g)}) stored at 20MPa in relatively large tanks that are potentially prone to leakage [1]). Moving to smaller satellites that are more sophisticated, both in terms of platform and payload capabilities, requires the availability of higher capability propulsion systems.

Better performance in propulsion can be achieved with monopropellant hydrazine (N₂H₄) that is fed to a catalyst, as suggested by the Jet Propulsion Lab, where it decomposes (e.g. over 29.7%Ir/Al₂O₃ or Fe-Co-Ni/Al₂O₃ [2]). Exothermic decomposition (e.g. N₂H₄ → N₂ + 2H₂ or less effective 3N₂H₄ → 4NH₃ + N₂) raises the catalyst temperature to say 1300K, causing an increase in fluid volume, exit velocity and thrust for essentially zero power initially supplied. However N₂H₄ is toxic and hazardous, resulting in high safety-related costs.

Nitrous oxide (N₂O) is an alternative and greener monopropellant [3]. It is non-toxic and stores as a liquid (0.75g/cm³) at around only 5MPa. SSC has been involved in the development of an N₂O microthruster with a specific impulse (Isp) of ≈150s (i.e. significantly above the 60s for N₂O as a cold gas). Its initial power requirement (below 31W) and simple design makes it attractive to smaller satellites. UoSAT-12 was launched at 6am on 21st April 1999, containing 2.5kg of N₂O that was sufficient for 14 h of resistojet propulsion [4]. During ground testing it was noted that N₂O decomposition could be self-sustaining. It was judged that a catalyst could lower the start up temperature (1073K). This catalyst would, however, need to be thermally stable and clean. For example, anthropogenic N₂O-derived NO [5] helps destroy stratospheric O₃. Hence N₂O use in satellites requires *clean and total* decomposition; no N₂O decomposition by-products must contribute to space weather [6].

While 7kg nanosatellites and 50kg microsatellites offer faster and cheaper access to space for a wider range of countries, their low cost orbit manoeuvres requires novel resistojet thrusters [7] with ever lower levels of input power required per unit of thrust produced. In this context a N₂O monopropellant thruster is particularly appealing. Such propulsion units based on green Co-Cu-Zn catalysts and N₂O could be key to the development of such new small satellites [4].

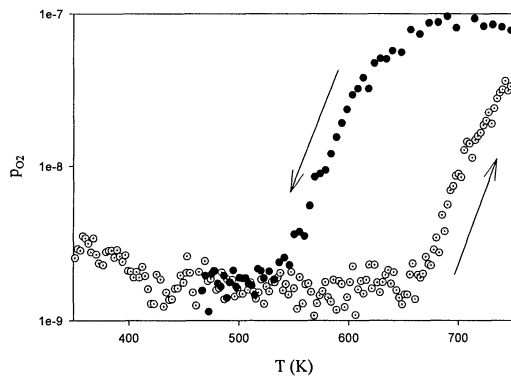


Figure 1. O₂ emerging on N₂O decomposition on EuroPt-1 6.3%Pt/SiO₂. 0-100% conversions are shown as an arbitrary p_{O2} scale.

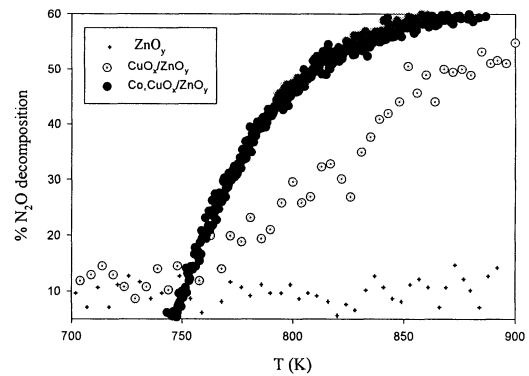


Figure 2. % N₂O decomposition over ZnO_y, 8%CuO_x/ZnO_y and 8%Co,4%CuO_x/ZnO_y

Work described here has been performed at UniS/Surrey Space Centre (SSC) and had the aim of producing methods of accelerating green Co-Cu-Zn catalyst evolution for a clean N₂O monopropellant microthruster that is active, stable and has its power requirement minimised (e.g. by UV irradiation).

(b) N₂O

N₂O is thermodynamically unstable (e.g. for its dissociation $\ln K = +42.0$ at 298K and $+18.8$ at 1000K), but is kinetically stable, since its bimolecular decomposition only takes place >838 K with an activation energy of 245-264kJ/mol [8], because the conversion is spin-forbidden. N₂O decomposition is exothermic. It is *catalysed* by a variety of surfaces [9]. Often the kinetic orders with respect to N₂O and O₂ have been found to be $+1.00$ and -0.5 , although retardation of the rate-determining step (O₂ release from the surface) by O_{2(g)} depends on catalyst pre-treatment. Metals and oxides [9] are active in N₂O decomposition at temperatures below those of the homogeneous bimolecular reaction. Since activation energies are lower on Rh₂O₃ (42kJ/mol) than Al₂O₃ (188kJ/mol), it is not surprising that spinel (e.g. Mg_xCo_{1-x}Co₂O₄ [9]) and oxide (e.g. ZrO₂ [10]) activity towards N₂O is increased when supporting Rh [9,11], Ru [12], Cu-Co [13] or Cu [14].

(c) Low Power Input Catalytic Microthrusters

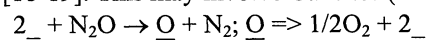
Solar mirrors have been used in high temperature materials processing [15]. Interestingly, the flux of UV radiation (e.g. UVA at 320-385nm and UVB at 290-320nm) rises with altitude from the Earth [16]. Many years ago, it was appreciated by Konstantin Tsiolkovsky that a focussed mirror on a spacecraft or satellite would produce a temperature of 5300-6300K.

The present authors have taken the first steps to determine whether a low power solar-thermal catalytic N₂O microthruster could be developed. Of course in other contexts, zero-power engines have been considered [17].

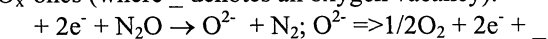
2. Experimental

(a) Catalyst

Cu/ZnO-based catalysts are active in methanol synthesis [18], methanol decomposition and the water-gas shift reaction. N₂O can ascertain their Cu surface areas through decomposition at 293-393K [18-19]. This may involve Cu⁰ sites (denoted $_$):



or CuO_x ones (where $_$ denotes an oxygen vacancy):



Experimentally these may be followed by frontal chromatography [20], subsequent reduction of O or O^{2-} [21] or other techniques [22]. Below 373K the decomposition is limited to surface Cu^+ formation [23], but others recommend even lower temperatures [24]. Certainly at 363K there is a weight increase in Cu/C during N_2O decomposition [25]. Here

ZnO_y
8% $\text{CuO}_x/\text{ZnO}_y$ and
8%Co,4% $\text{CuO}_x/\text{ZnO}_y$

were selected and prepared by precipitation as described previously [18-19]. ZnO is interesting being almost as thermally stable (i.e. 2248K m.pt.) as Al_2O_3 (2327K m.pt.) and stabilising the active sites (probably Cu^{x+}) in the support surface. It is also interesting in a photoactivation sense, being a semiconductor. Others [26] have compared $\text{CuO}_x/\text{ZrO}_2$ and $\text{CoO}_x/\text{ZrO}_2$ in N_2O decomposition and so 8% $\text{CuO}_x/\text{ZnO}_y$ and 8%Co,4% $\text{CuO}_x/\text{ZnO}_y$ were selected for initial study. XPS found 2p peaks (corrected to C1s at 285eV) in the Co, $\text{CuO}_x/\text{ZnO}_y$ (Co 794.3eV, Cu 952.2eV and Zn 1044.3eV) that corresponded to all metals in positive oxidation states in this mixed oxide catalyst.

(b) Catalytic Methods

N_2O decomposition has been followed using residual gas analysis (Sensorlab; RGA) over a sample (0.2g) of the catalyst (pre-dried at 723K) held in a purified $\text{N}_2\text{O}:\text{Ar}$ (1:3; $30\text{cm}^3/\text{min}$) stream during heating at 10K/min from 473K to 1073K. Products were analysed by RGA at m/e

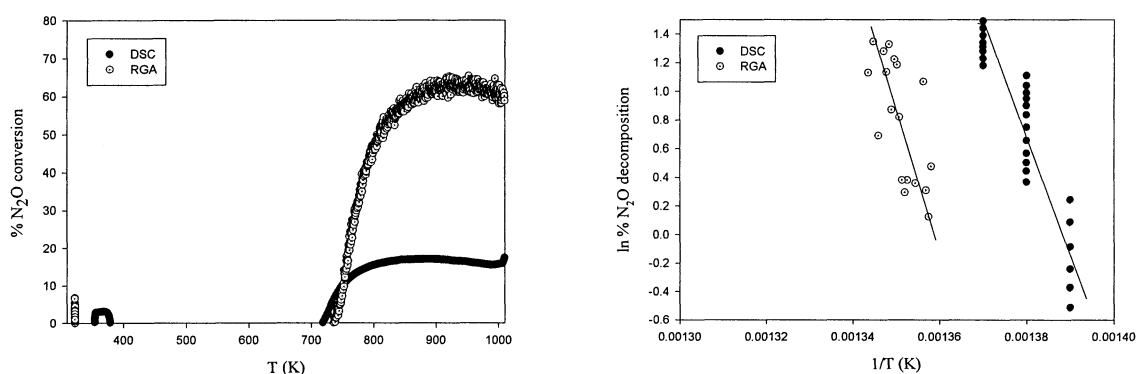


Figure 3. DSC and RGA analysis of N_2O decomposition on 8%Co,4% $\text{CuO}_x/\text{ZnO}_y$

equals 28 (N_2), 32 (O_2), 30, (NO), 44 (N_2O), 46 (NO_2) and 88 ($(\text{N}_2\text{O})_2$) as a function of time t . To check this method, EuroPt-1 Pt/ SiO_2 was used first. Interestingly, this showed substantial activity-temperature hysteresis (see Figure 1 [27]) in comparison with that seen in CO oxidation (-283kJ/mol), despite the fact that the decomposition of N_2O is less exothermic than CO oxidation, but then this is an insulator support.

Decomposition of N_2O pulses was also followed with catalysts (0.2g) in the dark or irradiated in the UV (Lot Oriel D-lamp ($200\text{nm} < \lambda < 500\text{nm}$)) at 473K in an Ar stream ($50\text{cm}^3/\text{min}$). Samples (0.1cm^3) of N_2O were injected. Analysis was as a function of time t after the injection (normalised by $t=0$ the time of injection and t_{max} the time to maximum RGA response to give $t/t_{\text{max}}=1$ at the point of maximum RGA response).

Calorimetric measurements of heat flows (i.e. dQ/dt in mW) have been used to measure rates of reaction over catalysts (on the assumption that the enthalpy of the reaction is temperature-independent [28]). Some have followed the catalysed decomposition of monopropellants via calorimetry [29]. Here a Setaram 121 differential scanning calorimeter (DSC) was used with the same $\text{N}_2\text{O}/\text{Ar}$ reactant stream flowing across the catalyst with simultaneous RGA analysis of products during temperature programming.

The 8% $\text{CuO}_x/\text{ZnO}_y$ sample was also tested in a microthruster test rig with input power (31W) to the electrical heater for the catalyst bed, the N_2O flow rate (dm^3/min) and lower and upper bed temperatures

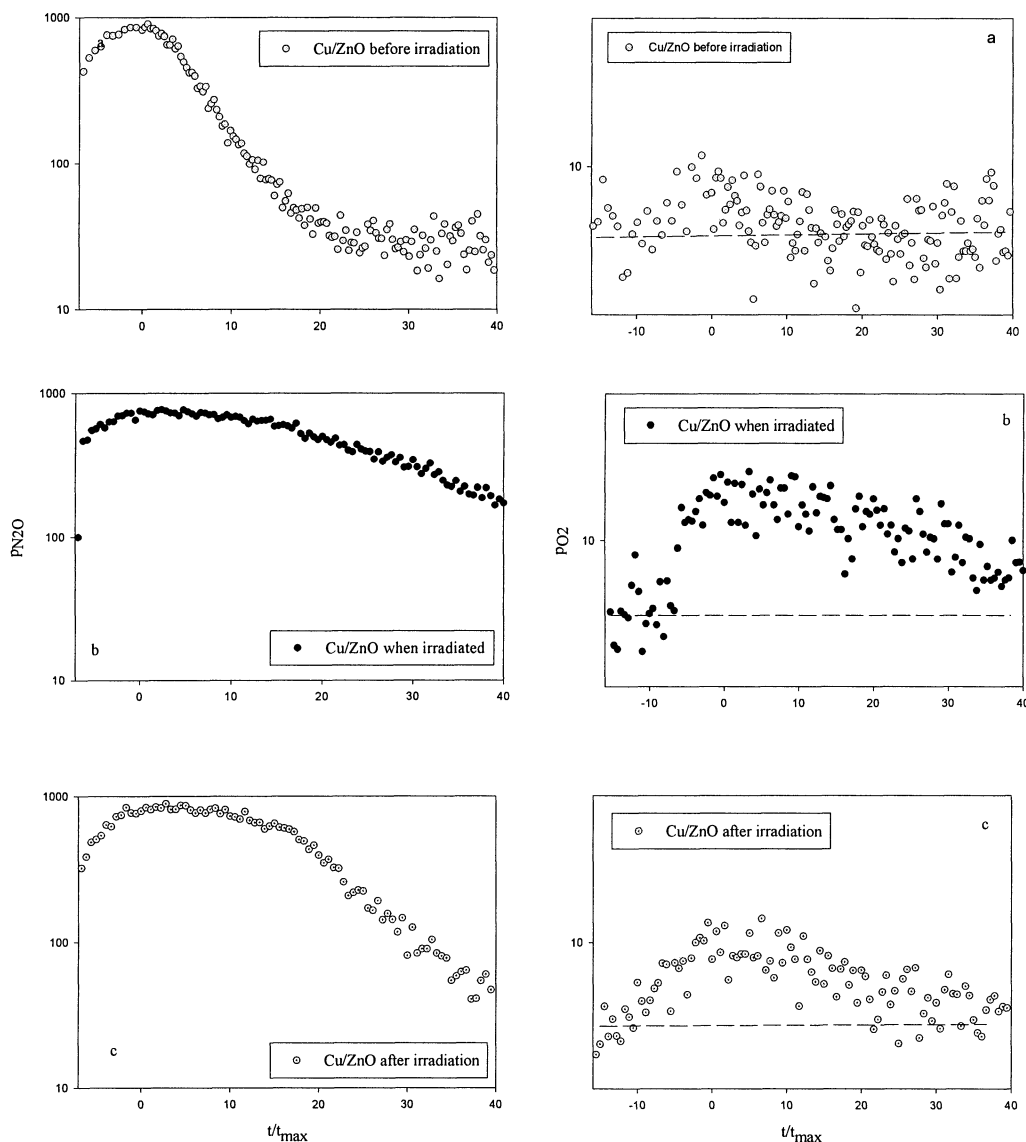


Figure 4. RGA analysis of N_2O pulses (left) and rates of O_2 release (right) with $8\%CuO_x/ZnO_y$ before (a), during (b) and after (c) UV irradiation, where p_{N_2O} and p_{O_2} have arbitrary units.

measured. The catalyst bed was initially heated electrically and then the dependence of the catalyst bed temperature on the N_2O flow was noted.

3. Results

Figure 2 shows that on heating $8\%CuO_x/ZnO_y$ and $8\%Co\%,4\%CuO_x/ZnO_y$ are, as expected, more active in N_2O decomposition than ZnO_y alone. Previously others [26] have seen 100% decomposition of $<1\%$ N_2O at $800K$ and $24000h^{-1}$ over $54-60m^2/g$ CuO_x/ZrO_2 and CoO_x/ZrO_2 ; the activation energies observed were $90-108kJ/mol$. Here this conversion level was seen below $750K$, making the present data at least comparable with previous data. The light-off temperature in N_2O decomposition [30] was estimated here as being at 5% N_2O conversion. These were in the sequence:

$$EuroPt-1 (670K) < Co,CuO_x/ZnO_y (679K) < CuO_x/ZnO_y (809K) < ZnO_y (\text{above } 1000K)$$

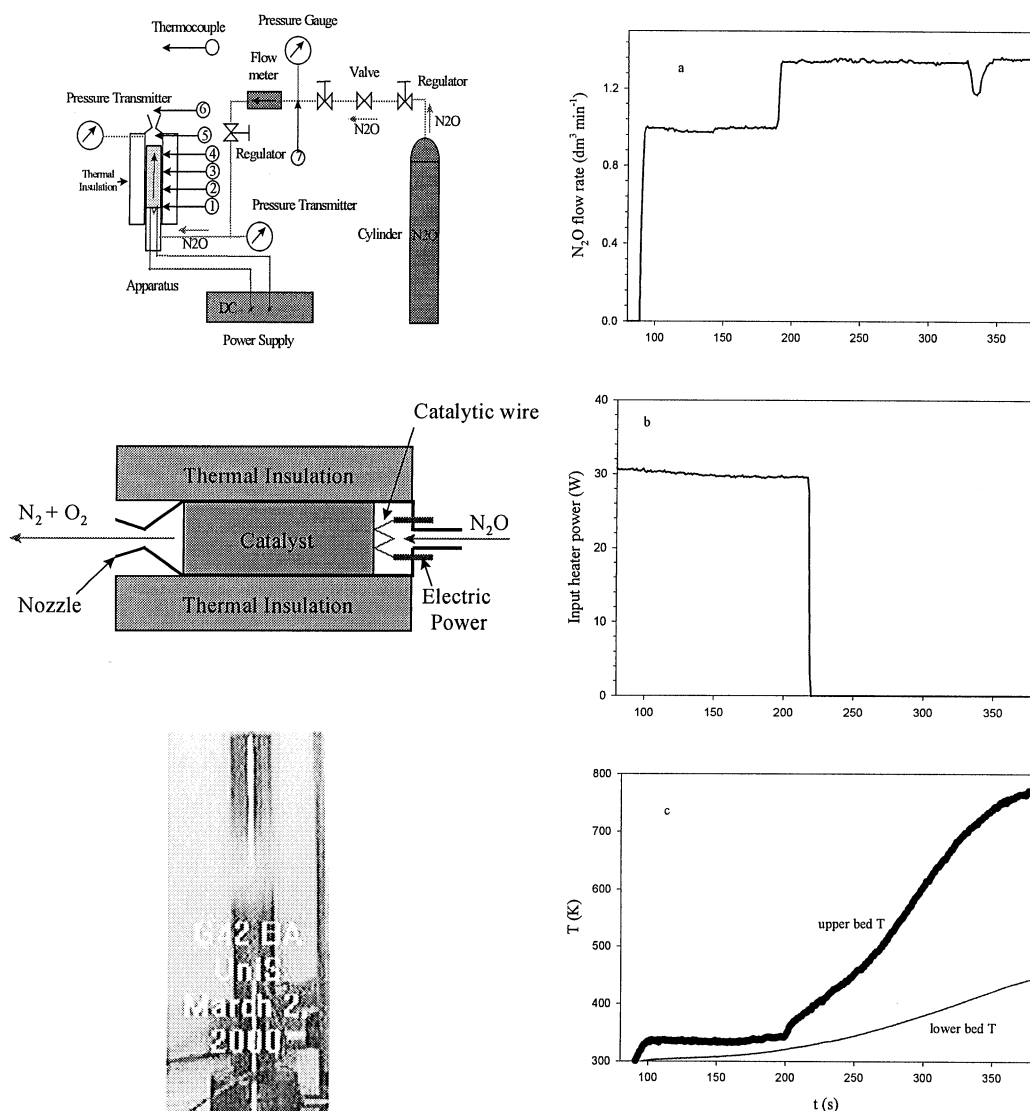


Figure 5. The left-hand side shows the gas handling system, the thruster-reactor and the glow from the thruster-reactor in use in N_2O decomposition. The right-hand side shows data for N_2O flow (a), input power supplied (b) and temperatures observed at the top and bottom of a $8\%CuO_x/ZnO_y$ bed in a reactor shown inset that was intended to simulate part of a microthruster operation. Later in the test the catalytic became entrained in the N_2O stream

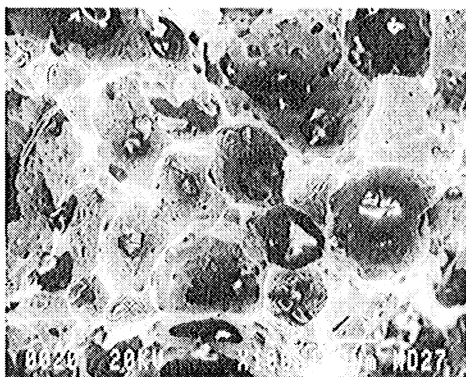


Figure 6. Scanning electron micrograph of a multicellular oxide foam that might be formed as a new catalytic

microthruster.

It was notable that on $\text{CuO}_x/\text{ZnO}_y$ and $\text{Co},\text{CoO}_x/\text{ZnO}_y$ (679K) the reaction was entirely selective to N_2 and O_2 , with no NO or NO_2 produced.

Figure 3 gives DSC and RGA evidence of N_2O decomposition on $8\%\text{Co},4\%\text{CuO}_x/\text{ZnO}_y$ (at lower temperatures than $8\%\text{CuO}_x/\text{ZnO}_y$). The figure also reveals that the DSC only sees a small fraction of the total amount of the heat liberated at any temperature. The fact that 100% conversion is not seen will depend on catalyst surface area and effective space velocities. A pseudo-Arrhenius analysis of RGA and DSC data gives an E_a in the range 20-21kJ/mol at about 5% conversion. This is very small, unless the reaction is transport limited.

Pulses of N_2O were broadened on the left-hand side of Figure 4 when the $8\%\text{CuO}_x/\text{ZnO}_y$ sample at only 473K (i.e. well below the light-off temperature of 809K) was irradiated (and also afterwards for a considerable period of time) and so enhancement of N_2O decomposition activity does not need irradiation to be continuous. More important was the evidence of O_2 liberation (also see the right-hand side of Figure 4). When N_2O pulses were introduced to the non-irradiated $8\%\text{CuO}_x/\text{ZnO}_y$ catalyst surface at 473K, no O_2 was liberated. However, during and after UV irradiation, O_2 was liberated. Hence the decomposition of N_2O with liberation of N_2 and $1/2\text{O}_2$ was photocatalysed at photon energies abundantly available to a catalyst in a satellite. However, since t_{max} was 20s, solar microthrusters of low electrical power input are more usable in a continuous (more than a pulse) mode. The irradiation would, however, not need to coincide with the decompositional propulsion.

In microthruster test experiments (see Figure 5) initially the bed of $8\%\text{CuO}_x/\text{ZnO}_y$ was heated electrically at 31W to about 330K. Then just over $1 \text{ dm}^3 \text{ N}_2\text{O}$ per minute was fed to the bed without a significant rise in the catalyst temperature. However, on raising the N_2O flow rate to $1.4 \text{ dm}^3/\text{min}$ the bed temperature rose to 760K. Eventually the experiment stopped when the catalyst was lost from the reactor in the N_2O stream. Clearly the catalyst works, but requires nano-engineering to make it work in a real microthruster.

4. Discussion

Can Catalysts be Nano-Engineered for Smaller Satellites? The surface areas and thermal stabilities of $\text{Co},\text{CuO}_x/\text{ZnO}_y$ are not yet ideal and sol-gel chemistry is being explored. Such catalysts could be produced in high area and castable forms. Possibly high porosity multicellular ZnO-based ceramics of the type shown in Figure 6 could be cast as integrated microthruster components in which the catalyst is incorporated in a variety of forms and shapes. This is to be explored at UniS/SSC. A p-type semiconductor like Cu_2O should be more active in N_2O decomposition than n-type ZnO because adsorption of excess O_2 is easier [24]. Thus the reaction is significant on Cu_2O at 493K and on ZnO at 673K. Nevertheless, it is not clear whether the activity really exists at the $\text{CuO}_x\text{-ZnO}_y$ interface. $\text{Co},\text{CoO}_x/\text{ZnO}_y$ is not novel as a catalyst composition, but for the moment it is allowing DSC-RGA methodologies to be evolved and it is much greener than say NiO-based catalysts, with all of their toxicity problems and higher E_a values [31].

Can DSC and RGA methods be combined to optimise these catalysts? The optimisation of these nanoengineered catalysts should involve DSC and RGA for analysis of steady-state, transient, hysteretic and oscillatory [32] activity, together with control of their deactivation with time t and use. These are all important properties in catalyst selection and optimisation for N_2O microthrusters to which DSC-RGA techniques can contribute. In addition, RGA will allow isotopic studies of the mechanism of N_2O decomposition with $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ [31] and extents of by-product formation. RGA-DSC UniS analyses need therefore to be integrated with real SSC N_2O microthruster testing.

Can catalysts be nano-engineered for smaller satellites with almost zero electrical energy requirement (like N_2H_4)? N_2O only undergoes homogeneous photolysis at wavelengths ($\lambda=193\text{nm}$) too low to be relevant here [33], but photocatalytic decomposition of N_2O is known [34]. ZnO absorbs in the UV at 300-400nm (its band gap on emission being 2.1eV) [35-36]. Photoconductivity, O_2 photoadsorption and O_2 photodesorption has been seen on ZnO, although

this decays 'very quickly once the exciting radiation is cut off', due to the recombination of electrons and holes [37]. Thus it is known that O₂ is released when ZnO is irradiated at its

absorption edge (385nm) at 298K [38]. That 8%CuO_x/ZnO_y releases O₂ on irradiation in the UV is not surprising, but the fact the photo-induced reactivity is retained after cutting off the irradiation is noteworthy and potentially useful in satellite microthruster technology.

5. Conclusions

The N₂O microthruster technology considered here is not as advanced as those based on Ag or Ir/Al₂O₃ [39]. For the moment it seems that there is interesting chemistry at this solid-state/catalytic Co,CuO_x/ZnO_y oxide-oxide interface with potential catalytic application to satellite propulsion based on N₂O catalytic decomposition in micro-thrusters [40]. Solar thermal propulsion has been considered [41]; solar initiation could be advantageous technically and intriguing fundamentally.

It is clear that this type of thruster would *not* be suitable for missions with significant minimum impulse bit requirements. The optimum mission requirement would be for long duration, steady-state firings, which require low thrust. This could typically be a major orbital change manoeuvre. Should minimum impulse bits be required, e.g. for attitude control, the N₂O system could include small cold gas thrusters for just these requirements. However to ensure the maximum performance, most of this green monopropellant should be used in the catalytic thruster [42]. DSC-RGA and nanotechnology methods all have a role in the development of environmentally-friendly catalysts for more efficient green N₂O microthrusters for smaller future satellites.

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