Exploring the effects of heat treatments on 2 wt.% Pd-Al_2O_3 for N_2O decomposition

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Abstract: N_2O is an extremely potent greenhouse gas with a lifetime of 150 years.[1] Consequently it is important to decompose N_2O before it is released into the atmosphere. The aim of this study is to decompose N_2O into N_2 and O_2 at temperatures ≤ 350 °C. In the current work, we have investigated the effects of repeated testing or repeated thermal pre-treatment on the activity of 2 wt.% Pd-Al_2O_3 catalyst. As the dissociation of N_2O releases oxygen which can effectively poison a metallic catalyst surface, we have also evaluated the effect of adding a hydrocarbon to the gas stream.

Keywords: Nitrous Oxide, Palladium, Alumina.

1. Introduction (11-point boldface)

There is an increasing awareness of the disproportionate negative impact of the minor pollutants released into the atmosphere. In the past, they have been seen as either too insignificant (e.g. N_2O) or too inert (e.g. CH_4) to be regulated, but increasingly their release is being targeted by legislation that is primarily aimed at reducing greenhouse gas emissions.

Although N_2O accounts for only 326 ppb of the atmosphere, [1] it has a global warming potential of 300 and an ozone depletion potential comparable to many HCFCs. [2] In fact, anthropogenic N_2O emissions are the single largest group of ozone-depleting gases that are released into the air. [3] Emissions from large centralised industrial sources (such as adipic acid and nitric acid plants [4]) are often effectively controlled, but the many small delocalised sources remain unregulated. The absence of legislation reflects the absence of suitable technology for eliminating N_2O on a small scale either at point of use (e.g. in hospitals and dental surgeries [5]) or when it is released as a part of a complex gas mixture (e.g. car exhaust).

The aim of this study is to decompose N_2O into N_2 and O_2 at temperatures ≤ 350 °C. In the current work, we have investigated the effects of repeated testing or repeated thermal pre-treatment on the activity of a 2 wt.% Pd-Al_2O_3 catalyst. As the dissociation of N_2O releases oxygen which can effectively poison a metallic catalyst surface, we have also evaluated the effect of adding a hydrocarbon to the gas stream.

2. Experimental (or Theoretical)

2 wt.% Pd-Al_2O_3 Catalyst was prepared by impregnation as follows; $PdCl_2$ was dissolved in water to give a solution with a concentration of 6 mg/mL. To this palladium solution (4 mL) γAl_2O_3 (0.98 g) was added and heated slowly to 55 °C until a slurry was formed. The slurry was then dried in an oven at 120 °C for 2 hours, and calcined at 600 °C for 4 hrs at 10 °C/min in flowing air. Further heat treatments carried out at 600 °C for an hour at 20 °C/min in flowing air.

N_2O decomposition reactions were performed at atmospheric pressure in a continuous flow fixed bed reactor. All outgoing gaseous products were analysed using an Agilent 7890B Gas Chromatograph (GC). The catalyst (60 mg) was pretreated in a flow of N_2 (87 %) and O_2 (13 %) with a total flow of 92 ml/min at 600 °C for 1 hour before catalytic testing was under taken. Catalytic reaction conditions are as follows, N_2O (1 %), He (99 %) or N_2O (1 %), propane (1 %), He (98 %) with a total flow of 100 ml/min leading to a GHSV of ca. 76000 h^{-1}. The temperature of the reaction was ramped from 300 to 600 °C in 50 °C intervals at a ramp rate of 6 °C/min with a hold at each temperature for 1 hour and a GC chromatograph created every 15 minutes, with the conversions calculated based on the consumption of N_2O and propane.

3. Results and discussion

H_2-TPR, SEM-EDX, BET, XRD, XPS and CO chemisorption, were used to characterize the catalysts. Interestingly, high conversion of N_2O (≥ 99%) was achieved at 400 °C on the 5th re-use of the 2 wt.% Pd-γAl_2O_3 catalyst as compared to 65 % over the fresh catalyst with propane present (Fig. 1). In the absence of propane much higher temperatures are required to achieve high conversions, similarly the used catalysts perform better. To investigate the improvements in N_2O conversion with reused catalysts the pre-treatment protocol was altered to replicate the heat cycle of a used catalyst. The catalyst underwent five heat-treatments under flowing air prior to the N_2O reaction and improvements in the conversion were noted, however, were not directly comparable to the re-used catalyst. To investigate the differences observed, XRD of the calcined catalysts was carried out (Fig. 2), the formation of crystalline PdO was found to occur at 600 °C following repeated use or heat-treatment. We considered that this species is critical to the improved N_2O conversions observed. To understand the relationship between the presence of PdO and efficient N_2O abatement, CO chemisorption was carried out.

CO chemisorption indicated that after 5 heat treatment cycles the average Pd crystallite size formed after reduction was 140 Å compared to the fresh catalyst with a Pd particle size of 6 Å. Although this catalyst had improved decomposition activity and contained crystalline PdO, its performance was not identical to the re- used catalyst, which had a post reaction particle size of 46 Å with a dispersion of 8 %. Therefore, both XRD (for detecting PdO) and CO chemisorption (for measuring post-reduction size of the metal particles) can provide diagnostic information.

In order to maximize the formation of larger post reduction Pd particles the support was pre-treated at 600 °C. Following metal deposition and calcination, the presence of crystalline PdO was confirmed by XRD (Fig. 2). The conversion of N_2O in the presence of propane was the highest observed at 95 % at 350 °C (Fig. 1). After reduction the particle size was measured at 21 Å with a dispersion 18 % which suggests that there is an optimum post reduction particle size for high activity. High resolution TEM will be used to investigate this further.

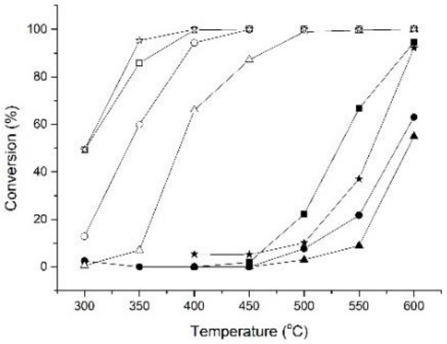

Figure 1. Graph showing the effect of heat treatments on 2wt%Pd-Al_2O_3 for N_2O decomposition. Reaction Conditions, Open symbols: 1:1:98 C_3H_8:N_2O:He total flow 100 ml/min, GHSV: 75900 h^{-1}. Closed symbols: 1:99 N_2O:He total flow 100 ml/min, GHSV: 76690 h^{-1} Legend: ▲ - 2 wt.% Pd-γAl_2O_3 fresh ● - 2 wt.% Pd-γAl_2O_3 5 heat treatments ■ - 2 wt.% Pd-γAl_2O_3 5 pre-treatments and uses, ★ - 2 wt.% Pd-γAl_2O_3 where the support was calcined at 600 °C before catalyst preparation.

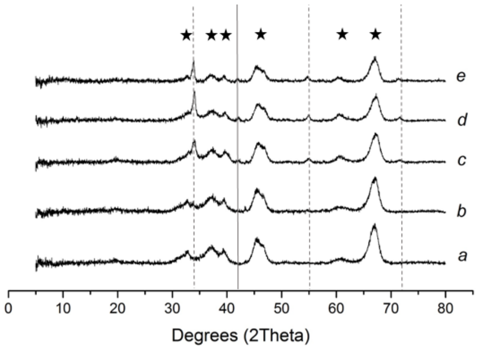

Figure 2. XRD data for 2 wt.% Pd-γAl_2O_3 series of catalysts and γAl_2O_3. *a* – Al_2O_3 fresh, *b* – 2 wt.% Pd-γAl_2O_3 calcined, *c* - 2 wt.% Pd-γAl_2O_3 used, *d* - 2 wt.% Pd-γAl_2O_3 5 heat treatments, *e* - 2 wt.% Pd-γAl_2O_3 where the support was calcined at 600 °C before catalyst preparation.
Legend dashed line – PdO, solid line – Pd, ★ - γAlumina

4. Conclusions

The decomposition of N_2O using 2 wt.% Pd-Al_2O_3 was studied and the activity and operating temperature of these catalysts was shown to be tunable *via* successive heat treatments and the use of an additional organic reductant respectively. After multiple cycles of pre-treatment and use of the palladium catalyst, the conversion of N_2O steadily increases. This effect can be mimicked by calcining the support before the palladium metal is introduced, therefore dramatically reducing the time required to obtain the highly active catalyst. The temperature required for 100 % conversion can also be lowered by the addition of a reductant to the gas stream. Here, the addition of propane resulted in a drop from > 600 °C to 350 °C. There is scope within this work to look at other reductants and their effect on the temperature required for total conversion. Initial testing focused on the use of methane, which is also a greenhouse gas. This resulted in a further decrease in the temperature required to achieve total conversion of N_2O to 300 °C. We suggest that these findings offer an interesting approach for the decomposition of two destructive gases using one reaction. Future work will focus on the further optimisation and understanding of the active catalyst along with attempts at lowering its operating temperature.

References

1 European Environment Agency, *www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-1#tab-chart_3*, 2015.
2 J. Weimann, *Best Pract. Res. Clin. Anaesthesiol.*, 2003, **17**, 47–61.
3 IPCC, *Climate Change 2007 Synthesis Report*, 2008.
4 J. Pérez-Ramírez, F. Kapteijn, K. Schöffel and J. A. Moulijn, *Appl. Catal. B Environ.*, 2003, **44**, 117–151.
5 S. S. Maroufi, M. J. Gharavi, M. Behnam and A. Samadikuchaksaraei, *Iran. J. Public Health*, 2011, **40**, 75–79.