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Characterisation of Robust Combustion Catalyst from Aluminium Foil Waste

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Abstract

Herein a robust and active combustion catalyst was prepared with three-quarter (75 wt.%) of its composition derived from the aluminium foil waste and designated as 5Pd-ACFL. The prepared catalyst was characterised using X-ray diffraction (XRD), Temperature-programmed reduction (TPR), Bright-field transmission electron microscopy (BF-TEM), High angle annular dark field (HAADF), Fourier transform infrared-pyridine (FTIR-Pyridine) and X-ray Photoelectron Spectroscopy (XPS) techniques and compared to the commercial equivalent (5Pd-AC550). The catalyst 5Pd-ACFL550 showed higher catalytic activity than that of 5Pd-AC550 in the total methane oxidation reaction with $T_{50\%}$ at 303 ºC at Gas hourly space velocity (GHSV) of 100,000 mL g^{-1} h^{-1}. Our approach opens doors for the preparation of robust cheap combustion catalyst from aluminium foil waste and demonstrates its application in the catalytic converters of natural gas vehicles (NGV-vehicles) and other combustion applications. As a result, this can be opened up to a wider variety of application markets, including residential and automotive applications.

1. Introduction

Aluminium oxide, alumina (Al_2O_3), is one of the most attractive ceramic materials for its various applications due to its thermal, chemical and mechanical stability.[1] For example, it is used as a catalyst support, adsorbent, ion exchangers, abrasives, in electronic device fabrication, filter, as a cutting tool material, or as an alternative for surgical material for implants.[2] Al_2O_3 exists in a range of metastable structures, the so-called transition aluminas, e.g. χ, k, γ, δ, η, ϴ as well as its stable α-Al_2O_3 corundum phase. This polymorphism can be classified in terms of the oxygen sublattice structure (OSS) and the distribution of Al^{3+} in tetrahedral and octahedral interstitial sites.[1a] Thus, in α-Al_2O_3 (trigonal), the OSS is hexagonal close-packed (hcp) structured with 2/3 of the octahedral sites occupied by cations, while γ, δ (either tetragonal or orthorhombic), η (cubic), ϴ (monoclinic) have a face-centered cubic (fcc) arrangement of oxygen anions and Al cations present in various proportions in both octahedral and tetrahedral sites. It has been established that boehmite transforms into stable α-Al_2O_3 via the following sequence.[1a]

$$AlO(OH) \rightarrow \gamma \rightarrow \delta \rightarrow \Theta \rightarrow \alpha \text{-} Al_2O_3$$
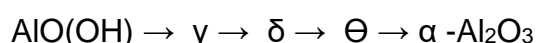
Al_2O_3 can be prepared in different phases, for instance, the dehydration of boehmite at 300-500 °C yields γ-Al_2O_3, while in a temperature range of 700-800 °C it produces δ-Al_2O_3, at a higher temperature range of 900-1000 °C it gives ϴ-Al_2O_3, and at 1000-1200 °C, α-Al_2O_3 is produced.[2] Among the various crystalline phases of alumina, γ-Al_2O_3 has received much attention due to a reduced generation of by-products.[3] Nonporous crystalline γ-Al_2O_3 has been widely used as a support in catalytic processes, such as polymerization, reforming, oxy-reforming, dehydration, hydrogenation and in the synthesis of biodiesel.[4] It offers good surface characteristics in heterogeneous catalysis, such as large specific surface area, pore size, pore

volume and a highly active site concentration on its surface. Usually, Alumina support is produced from bauxite ore, which is mined in countries such as West Africa, the West Indies and Australia. It causes massive environmental damage by generating considerable levels of waste such as tailings, red mud, emissions of perfluorocarbon and CO_2 gases during the production process.

In a previous work, a novel, eco-friendly synthesis of mesoporous alumina catalyst (γ-Al_2O_3) was performed from aluminium foil waste (AFW) with surface and bulk characteristics better than commercial alumina in term of the surface structure (morphology, surface area and pore volume) along with the surface acidity.[5] Our approach could decrease the quantity of AFW whereas avoids the environmental damage related with mining bauxite, the primary ore of aluminium, that's necessary to meet ever increasing the global aluminium consumption. In order to prepare 1 Kg of alumina catalyst, ~530 gm of the AFW is needed along with about 9L of HCl (30%w/w) and 9L of ammonia solution (30% solution) with a total cost of £120 per Kg of the alumina catalyst. The average cost of the commercial alumina catalyst is about £305 per Kg, so this novel idea can make a highly active catalyst with less than half the cost of the commercial alumina catalyst. However, in commercial alumina production, besides raw material cost, there is also labour cost, equipment cost, etc, which should be also considered.

One of the applications of the modified γ-Al_2O_3 is in the total methane oxidation (TMO) as a catalyst support. Recently, the bimetallic Pd-Pt loaded on a dual component support showed superior activity in the TMO reaction of palladium being the most active component and platinum enhanced the stability of the palladium species in the catalyst composition (5%Pd+2% Pt/17.5% TiO_2/ZSM-5 (80)).[6] It is well known that the acidic support is crucial for the TMO reaction as it makes the Pd metal more electron

deficient and enhances the re-oxidation of Pd(0) during Pd(0)/PdO redox cycle, consequently improving the catalytic activity.[6-7] The role for the oxygen storage (TiO_2) is to improve the oxygen mobility along with facilitating the reduction of the Pd species during the redox cycle in the TMO reaction and consequently improve the catalytic performance. Lin et al.[7] reported a decrease of $T_{10\%}$ by 30 °C on the addition of titania in the catalyst composition of (Pd/TiO_2/Al_2O_3), where $T_{10\%}$>250 °C, GHSV=33,000 mL h^{-1} g^{-1}. Miller et al.[8] studied the effect of the support on the palladium species for the TMO reaction and found that the activity results showed the following sequence Pd/Al_2O_3 > Pd/Ce-Zr > Pd/Ce.

The above discussion leads to the conclusion that converting AFW into mesoporous γ-Al_2O_3 (catalyst/support) using a cost-effective green synthetic route is highly desirable. Recently, we demonstrated a novel, eco-friendly synthesis of mesoporous γ-Al_2O_3 from AFW (ACFL550) with surface and bulk characteristics better than commercial γ-Al_2O_3 (AC550). Herein, we propose a robust combustion catalyst derived from the bimetallic Pd-Pt metals loaded on γ-Al_2O_3 that produced from AFW.

The preparation and characterisation techniques are shown in the supplementary.

2. Results and Discussion

2.1 Characterisation of pure catalysts derived from the ultrapure single crystals

The crystallite size calculated by the Scherrer equation showed that pure ACFL550 and AC550 have relatively similar crystallite sizes as shown in Table 1. The adsorption/desorption isotherm of pure ACFL550 is shown in Figure S1, demonstrating it is a type IV isotherm which is typically attributed to the mesoporous structure. X-ray single crystal of a trigonal crystal system with a space group of R-3c of homemade aluminium chloride hexahydrate derived from AFW is shown in Figure 1.
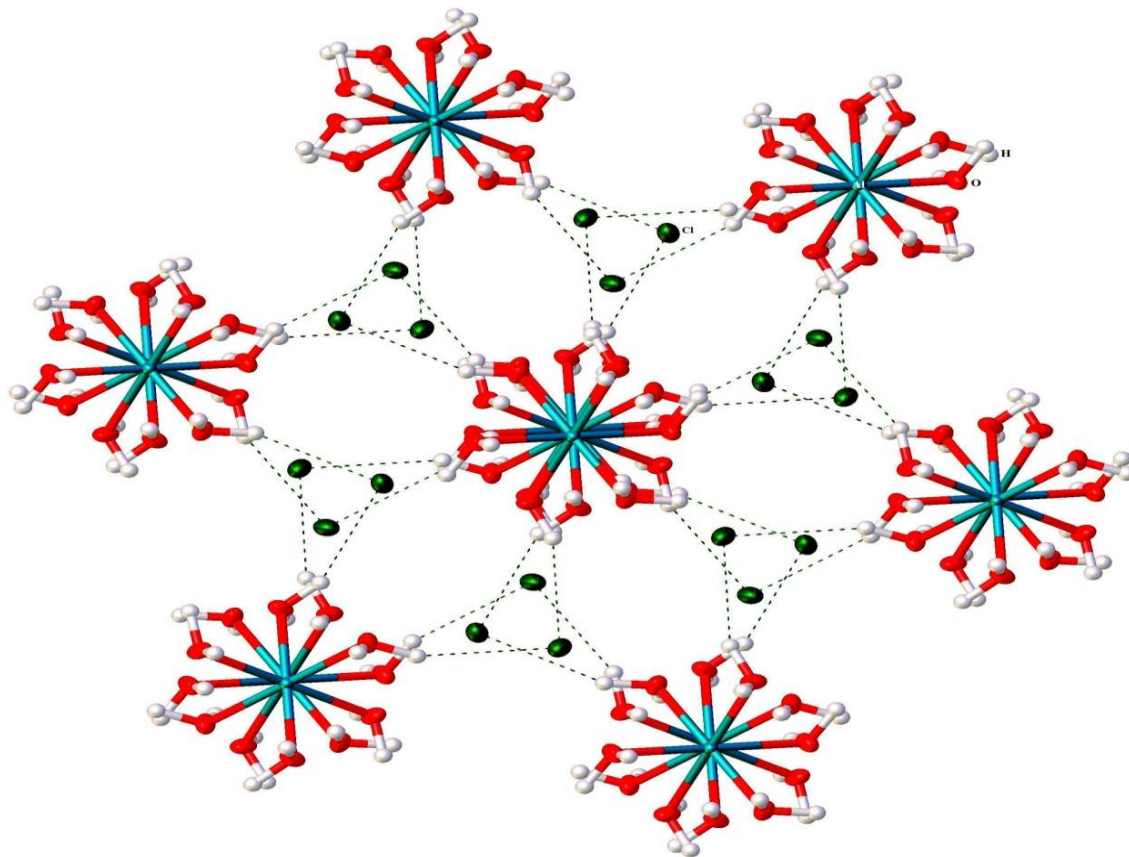
Figure 1: X-ray single crystal of homemade aluminium chloride hexahydrate depict the packing cubic crystal structure viewed along [001].

Table 1: shows the surface area (S_{BET} (m^2 g^{-1})), acidity and pore volume (cm^3 g^{-1}) for different acidic supports and their catalyst prepared.

| Support / Catalyst	S_{BET} (m^2 g^{-1})	Crystallite size (nm)	Pore volume (cm^3 g^{-1})	Total acidity[a], A(sites/g)	Acid density[b], B(sites/m^2)
ACFL120	387	3.0	0.36	-	-
AC120	378	3.1	0.20	-	-
ACFL550	300	3.5	0.45	7.01	2.4
AC550	278	3.7	0.35	6.91	2.5
5Pd-ACFL550	254	13	0.32	--	--
5Pd-AC550	233	15	0.22	--	--
93% TiO_2	107	51	0.27	--	--

[a] Total acidity = A x 10^{20}.

[b] Acid density = B x 10^{18}.

2.2. Characterisation of 5Pd- ACFL550 and 5Pd-AC550 used for the TMO reaction

The S_{BET} and the pore volume of the modified catalysts (5Pd-ACFL550, 5Pd-AC550 and 93%TiO_2 catalysts) are shown in Table 1, which reflect the surface area of the supports that were used during the preparation where 5Pd-ACFL550 catalyst has the highest surface area whereas 93% TiO_2 catalyst showed the lowest surface area. The XRD of these modified catalysts along with the supports is shown in Figure 2. The diffraction lines of TiO_2 that correspond to the anatase phase (JCPDS 21-1272) appeared in all the prepared catalysts. The diffraction peak at 2θ= 33.8 is attributed to the PdO phase,[6] with a larger peak in 5Pd-ACFL550 catalyst than that of 5Pd-AC550 catalyst and the 93% TiO_2 catalyst, where the peak is less visible, implying the formation of palladium oxide species on the surface of the 5Pd-ACFL550 catalyst was the highest among the modified catalysts.
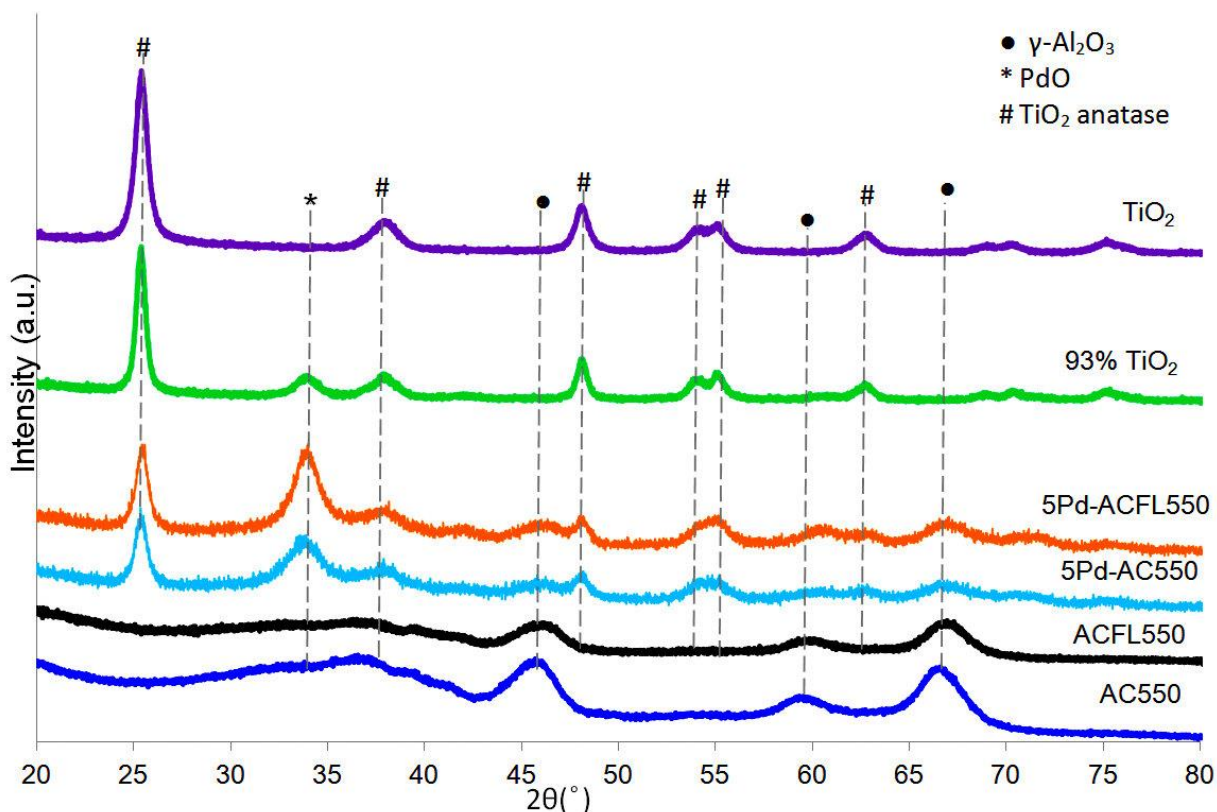
Figure 2: XRD patterns of the modified catalysts, 5Pd-AC550, 5Pd-ACFL550 and 93% TiO2 catalysts along with the supports used during the preparation (AC550 (commercial aluminium chloride), ACFL550 (AFW) and TiO2 supports).

The surface oxides of the modified catalysts were investigated using XPS analysis. Survey spectra of all three catalysts; 5Pd-ACFL550, 5Pd-AC550 and 93%TiO2 showed the presence of both Pt and Pd (Figure S2 (a)). Figures 3 and S2 (b) show high-resolution spectra of Pd *3d,* Pt *4f*, O *1s* and *Ti 2p*, The palladium species predominantly exist as PdO with binding energies of approximately 336.6 eV (Pd*3d*$_{5/2}$) and 342.3 eV (Pd*3d*$_{3/2}$) along with a small contribution of PdO2 at higher binding energy,[9] as seen in Figure 3 (a). Platinum *4f* region overlaps with Al *2p* as shown in Figure 3(b) for samples with Al2O3. However, these can be compared with Pt *4f* of 93%TiO2 catalyst which has no aluminium and it is seen that Pt *4f* $_{7/2}$ peak for all three catalysts appear at 71.8 eV which can be attributed to Pt (0) state and a minor contribution from Pt (+2) at a higher energy of approximately 73 eV.[10] The O *1s*

spectrum can be fitted with component peaks to show the existence of the related oxygens from the metal oxides (PdO, PdO$_2$, TiO$_2$ or Al$_2$O$_3$) and hydroxides at binding energies approximately 529- 531.5 and 533.1 eV, respectively as seen in Figure 3(c).

 It is not surprising that 93% TiO$_2$ catalyst showed the largest Ti $2p_{3/2}$ peak among the modified catalysts (Figure S2 (b)) and this is attributed to the higher TiO$_2$ content in the catalyst composition (93 wt.%) compared to 17.5 wt.% for the other catalysts.[11]
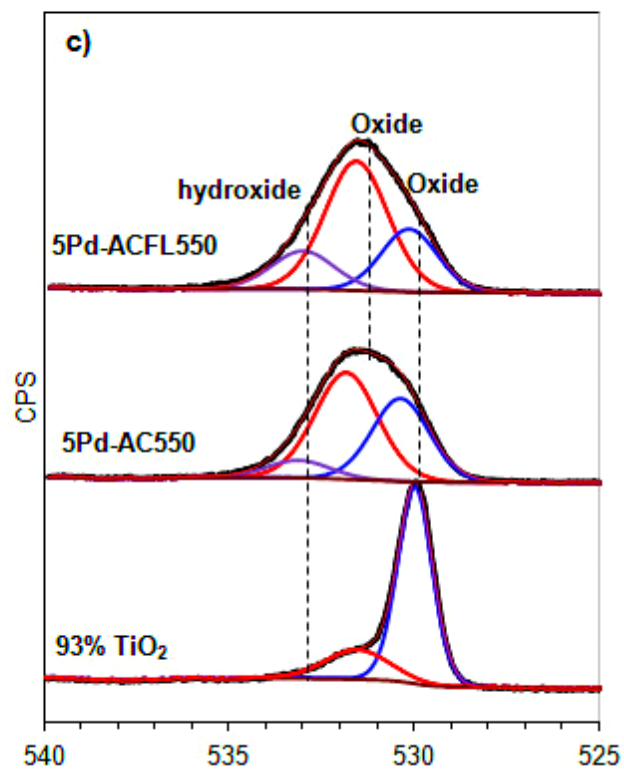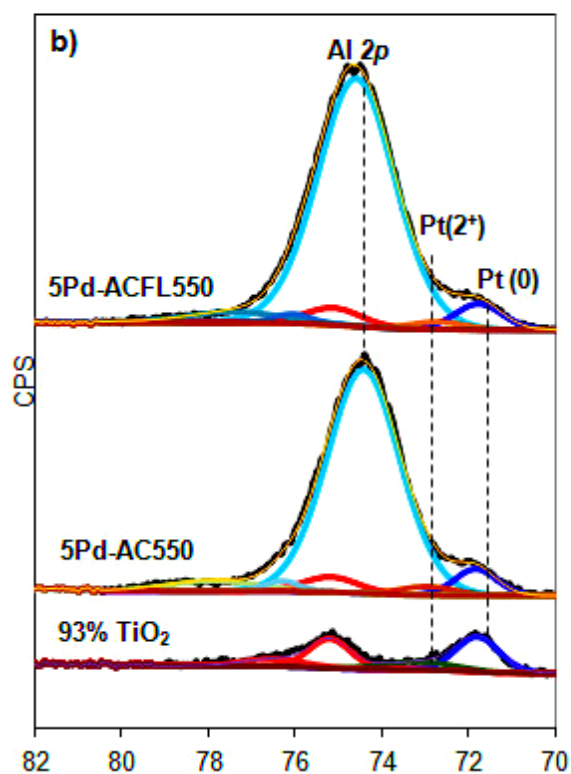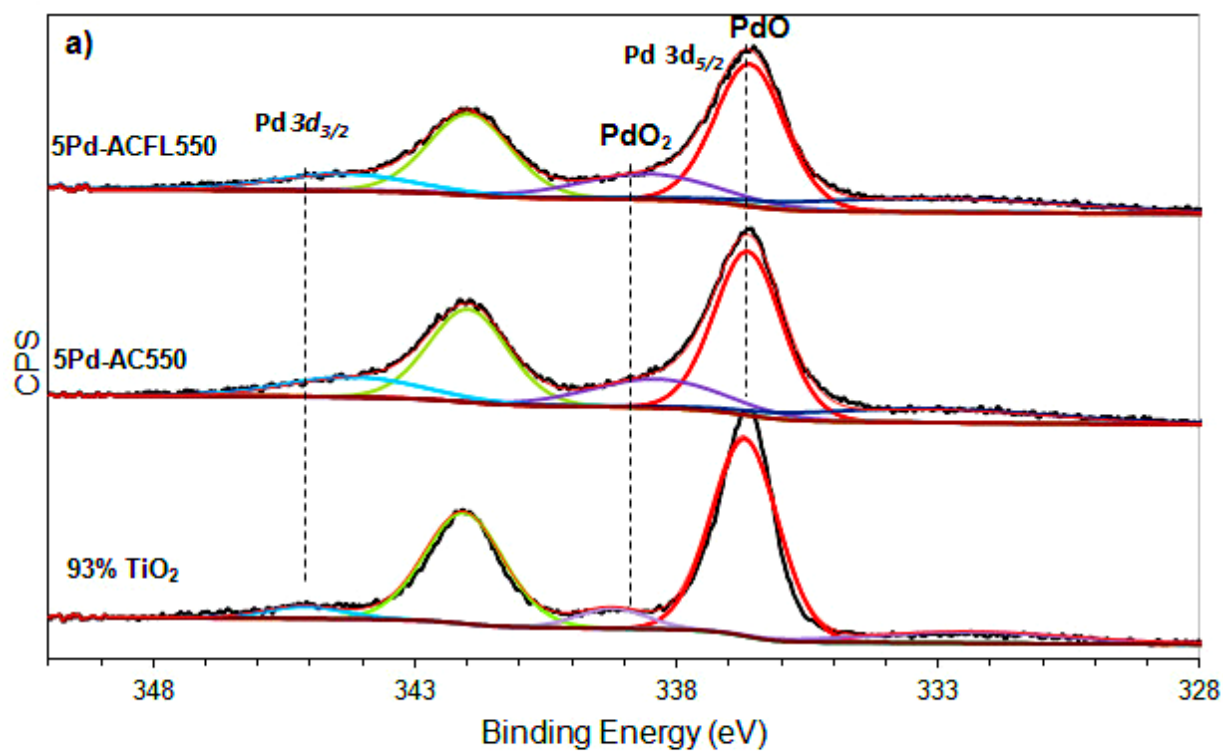
Figure 3: XPS of 5Pd-ACFL550, 5Pd-AC550 and 93% TiO₂ catalysts a) Pd *3d*, b) Pt *4f* and c) O *1s*.

The pure ACFL550 catalyst showed nano-rod particles of less than 10 nm in size as shown in a previous work.[5] TEM analysis of the 5Pd-ACFL550 catalyst is shown in Figure 4(a-c), where image (a) and (b) show the transmission electron micrographs of the catalyst in bright field and STEM modes, respectively, wherein the HAADF the bimetallic (Pd/Pt) and TiO_2 appears to be located in regions of brighter contrast. Figure 4 (c) shows elemental maps acquired by STEM-EDX of the principle elements in the 5Pd-ACFL550 catalyst. As expected, the alumina structure is dominant, with Ti found around the edges. The Pd and Pt signals are similar to each other, dispersed across the support structure with a fairly random distribution. The particle size of the palladium was around 13 nm as shown in Figure S3 (c).
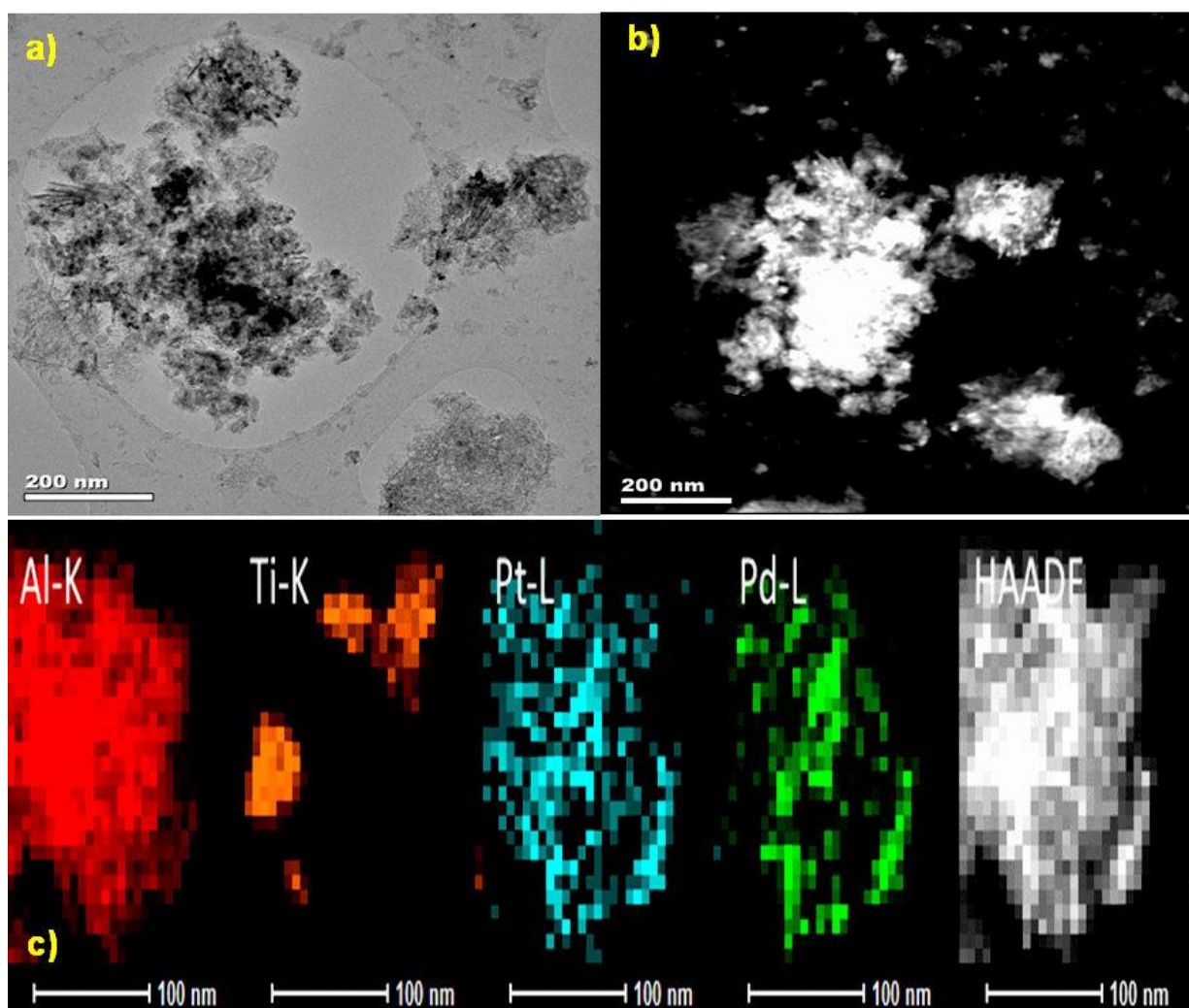
Figure 4: TEM overview image a) and b) show TEM-BF of the 5Pd-ACFL550 catalyst in bright field and STEM modes, respectively. Image c) shows the EDX spectral images taken from the 5Pd-ACFL550 catalyst of the Al-K, Ti-K, Pd-L and Pt-L peaks.

The enhanced reducibility of the catalyst is a crucial criterion during the redox cycle in the combustion reaction.[6] The H_2-TPR spectra of 5Pd-ACFL550 and 93% TiO_2 catalysts along with the supports (ACFL550 and TiO_2 supports) are shown in Figure 5 and show the influence of the support on the palladium species. No reduction peak is seen for the ACFL550 support whereas the titania oxide support showed a broad reduction peak in the temperature range of 330-550 ºC, which is attributed to the

reduction of Ti^{4+} to Ti^{3},[6] where this peak was shifted to lower reduction temperature (200-400 ℃) in 5Pd-ACFL550 and 93% TiO_2 catalysts. This implies that the reducibility of TiO_2 was enhanced with the metals and the alumina support. Osman et al.,[6] showed that TiO_2 enhanced the reducibility of the palladium species while the acidic support (alumina) increased the electrophilicity of the Pd species and consequently enhanced the re-oxidation of the catalyst. With high TiO_2 loading as in 93% TiO_2 catalyst the palladium species are more readily reducible and as a result, a negative peak was observed around 38 °C. This is attributed to the β-hydride of the palladium metal Pd (0) and only appeared in that catalyst along with a positive reduction peak around 1 °C which is attributed to the PdO phase. Catalyst 5Pd-ACFL550 showed two positive reduction peaks for the PdO species around 1 and 80 °C, this is due to the catalyst composition which is mainly acidic support (75.5 wt.%) that enhanced the re-oxidation of the palladium species over the surface of the catalyst. These results are in agreement with the XRD results where 5Pd-ACFL550 catalyst showed the highest PdO diffraction peak while 93% TiO_2 showed the smallest PdO diffraction peak. However, 93% TiO_2 catalyst showed facile reduction behaviour, there was a poor dispersion of the metals on the surface and led to the formation of big clusters as shown in Figure S4. The maps showed high agglomeration of Ti, Pd and O and slightly less of Pt species on the surface of the catalyst which was confirmed by the XPS results as predominantly Pt metal phase (Figure 3(b)).
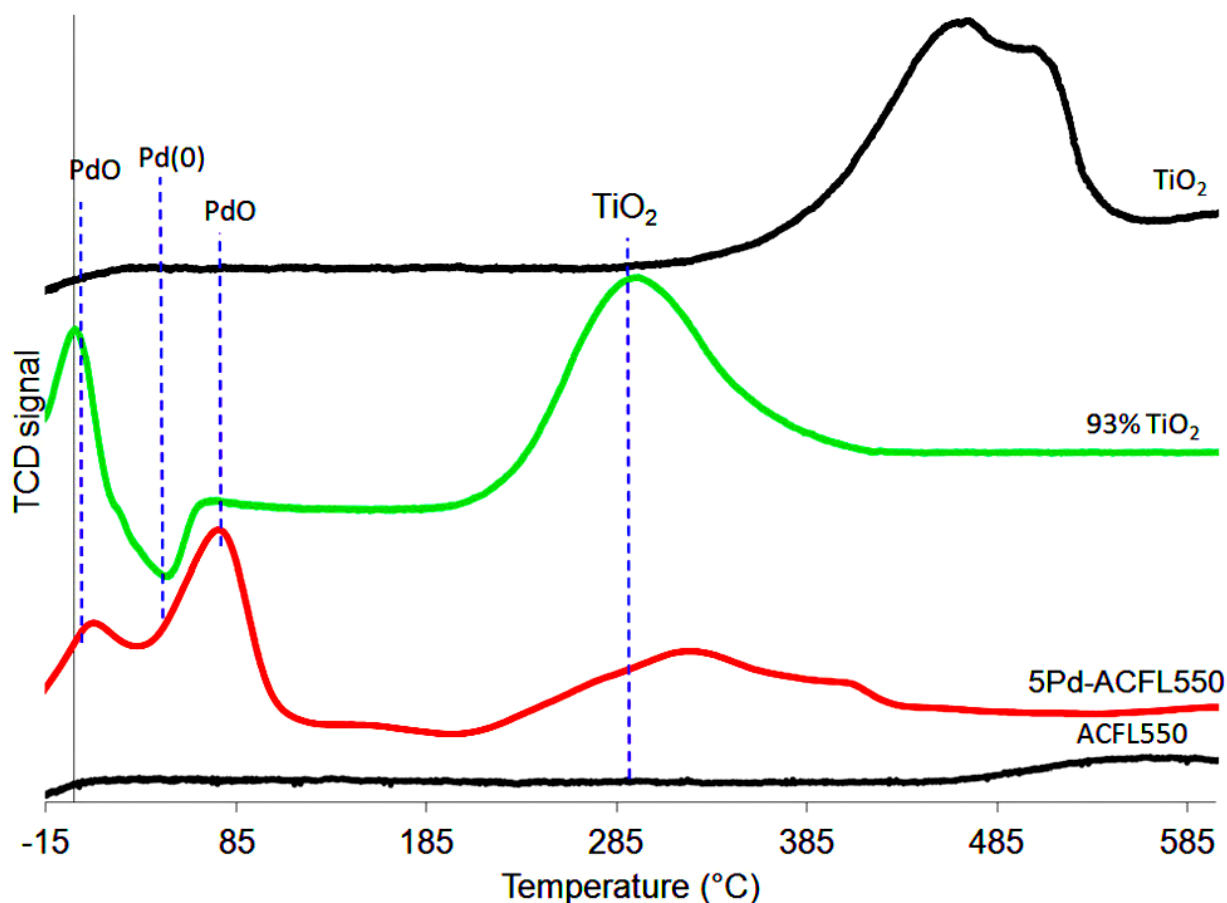
Figure 5: TPR spectra of 5Pd-ACFL550 and 93% TiO₂ catalysts along with the supports used during the preparation (ACFL550 and TiO₂ supports).

The FTIR pyridine spectra of the 5Pd-ACFL550 catalyst along with the supports of ACFL550 and TiO₂ are shown in Figure S5. The surface acidity of the ACFL550 support was slightly changed upon deposition of Pd, Pt and TIO₂ with Lewis acidic sites being the dominating acidic sites on the surface of the catalyst. It is obvious that the TiO₂ support showed the smallest amount of Lewis acidic peaks among these catalysts.

3. Catalyst applications in acid-catalysed reactions

3.1 The total methane oxidation reaction

The catalytic activity tests were performed elsewhere,[5] and it was obvious that the catalysts that have acidic support component (5Pd-ACFL550 and 5Pd-AC550) showed higher catalytic activity than that of the mono-component support, without acidic support, (93% TiO_2). The lower catalytic activity in the 93% TiO_2 catalyst is due to the absence of the acidic support in the catalyst composition. The catalytic activity of 5Pd-ACFL550 (derived from AFW) catalyst was apparently higher than that of 5Pd-AC550 (derived from the Al chloride precursor) and 93% TiO_2 catalysts with $T_{50\%}$ at 303, 321 and 340 ºC, respectively. The superior catalytic activity of 5Pd-ACFL550 compared to 5Pd-AC550 may be due to the stronger Lewis acidic sites in the ACFL550 than the AC550 supports as shown in the FTIR-pyridine and TPD-Pyridine as well as the higher surface area and bigger pore volume as seen in Table 1. Furthermore, the chlorine contents are known to block the active sites on the catalyst surface and consequently lead to catalytic deactivation.[7, 12] EDX analysis showed that the % Cl in ACFL550 is half that of AC550 with 1.8 and 3.8, respectively (not shown). Thus, it is not surprising that 5Pd-ACFL550 showed a higher catalytic activity than that of 5Pd-AC550 in the TMO reaction. The time on stream test for the 5Pd-ACFL550 catalyst showed a good stability during the 50 hrs TOS test.

4. Conclusions

Herein, we characterise a robust combustion catalyst derived from AFW with high activity in the TMO reaction with $T_{50\%}$ at 303 ℃. Four components are needed for a highly active methane combustion catalyst. Palladium as the active metal species, platinum to stabilise the palladium, TiO_2 as an oxygen carrier to ensure a good supply of oxygen and γ-Al_2O_3 (derived from AFW) as an acidic support to activate the methane and increase the electrophilicity of palladium, hence the re-oxidation during the redox cycle in the TMO reaction. All components are needed to work together to achieve optimum activity and stability. STEM-EDX of the most active catalyst (5Pd-ACFL550) showed that the catalyst structure is dominated by alumina, with Ti found around the edges. The bimetallic Pd-Pt metals are similar to each other, dispersed across the support structure with a fairly random distribution. These results open doors for the preparation of highly active and well-structured nano-mesoporous alumina catalyst/support from AFW and its application in acid catalysed reactions and especially in combustion reactions.

Supporting Information Summary

Experimental section and catalyst characterisation techniques along with the following figures (SBET, XPS, TEM, SEM/EDX and FTIR-Pyridine spectra).

Competing financial interests: The authors declare no competing financial interests.

Keywords: aluminium foil, aluminium waste, combustion catalyst, γ-Al_2O_3, Palladium, total methane oxidation.

5. References

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Table of Contents text

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TOC: