N₂O has been widely recognized as a hazardous greenhouse gas exhibiting 300 times higher Global Warming Potential compared to CO₂, as well as an ozone layer destruction contributor. One of its major sources is fossil fuels and biomass combustion and, consequently, several methodologies have been considered towards its end-of-pipe emission control. Catalytic decomposition represents the most promising method, due to lower energy demand and cost. Currently, Ir-based catalysts have gained considerable interest as promising alternatives for de-N₂O process. Enhancement of the Ir active phase intrinsic features via support-mediated promotional effects comprises the subject of the present study. In particular, the effect of Ce₀.₈La₀.₂O₁.₉-modified γ-Al₂O₃ support (AlCeLa) on the Ir nanostructural characteristics and its de-N₂O activity is investigated, using a combination of electron microscopy (TEM, HRTEM) and image analysis methods.

The morphology of the unmodified 0.5 wt.% Ir/γ-Al₂O₃ sample is depicted in Fig. 1. IrO₂ catalyst adopts both a medium-size (up to 70 nm), crystalline rectangular particle morphology (a), as evidenced by the Selected Area Diffraction (SAD) pattern in (b), and a smaller and disordered particles one (c), densely aggregated on top of γ-Al₂O₃. Supporting Ir on AlCeLa results in the exclusive formation of larger size, highly crystalline IrO₂ particles, as illustrated in Fig. 2(a) and (b), although the Ir loading is identical in both catalysts. The particles’ mean size is up to 500 nm in Ir/AlCeLa. Their high crystalline quality is presented in Fig. 3(a), where the edge of a IrO₂ particle is shown, viewed along its [001] zone axis. Measurements of the lattice spacings resolved in the image resulted in d₁₁₀=0.317 nm and d₂₀₀=0.223 nm, in good agreement with their theoretical values. This is further confirmed by the Geometric Phase Analysis (GPA) results in Fig. 3(b). The strain map reveals a uniform distribution, even at the surface crystal edges, where any contamination by impurity elements or crystal defects formation may be more pronounced. Strain leaps, white arrowed in Fig. 3, were only measured at regions of crystal misorientations due to particle inclination.

The superior structural quality of Ir/AlCeLa catalyst was reflected in its outstanding ~100% and 90% N₂O conversion records, in the absence and presence of O₂, respectively. This is most probably a result of the trend of oxygen, formed by N₂O decomposition, to desorb more easily from highly crystalline, clear IrO₂ surfaces rather than from defected cites, mainly present in disordered, poorly crystalline small Ir particles. This inevitably leads to higher N₂O decomposition activity in the former case, rendering Ir/AlCeLa a highly efficient de-N₂O catalyst.

Acknowledgement: Financial support by the program “THALES” (MIS 375643), co-financed by the Greek Ministry of Education and Religious Affairs and the European Social Fund is acknowledged.
Fig. 1: (a) and (c) TEM images from the Ir/γ-Al₂O₃ catalyst, revealing the two distinct morphologies; (b) typical SAD pattern from the area in (a). Reflections attributed to IrO₂ are denoted in (b).

Fig. 2: (a) TEM image and (b) [001] SAD pattern of a typical IrO₂ particle in the Ir/AlCeLa catalyst. The difference in size and crystallinity is outlined.

Fig. 3: (a) HRTEM image, viewed along [001] and corresponding GPA strain map (b) from the edge of an IrO₂ particle in the Ir/AlCeLa catalyst. A uniform distribution of strain is illustrated; peaks are only observed at regions of crystal inclination, as shown by the strain profile inset in (b).