Commercial and laboratory-prepared V_2O_5-WO_3/TiO_2-based catalysts with different compositions were tested for catalytic decomposition of chlorobenzene (ClBz) in simulated waste combustion flue gas. Resonance enhanced multiphoton ionisation-time of flight mass spectrometry (REMPI-TOFMS) was employed to measure real-time trace concentrations of ClBz contained in the flue gas before and after use of the catalyst. The results showed that the ClBz decomposition efficiency was significantly enhanced when nano-TiO_2 instead of conventional TiO_2 was used as the catalyst support. No promotion effects were found in the ClBz decomposition process when the catalysts were wet-impregnated with CuO and CeO_2. A comparison between ClBz and benzene decomposition on the V_2O_5-WO_3/TiO_2-based catalyst showed that different active sites were likely involved in the decomposition mechanism, and the V=O and V-O-Ti groups may only work to catalyse the degradation of the phenyl group and the benzene ring rather than the C-Cl bond.