

Single-site photocatalytic solids for the decomposition of undesirable molecules†

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Photocatalytic solids, in which the absorption occurs at isolated, spatially well-separated centres, are particularly useful catalysts for effecting reactions that are of prime importance in both remedial and preparative contexts. These are qualities that they share with single-site (thermally-activated) heterogeneous catalysts; but they have the added advantage of being more readily probed during the actual processes of catalytic turnover, since they generally function under ambient conditions, unlike most conventional solid catalysts which usually operate at elevated pressures and temperatures. Thus, they are amenable to investigation by (*in situ*) X-ray absorption (XAFS), FT-IR, UV-Vis, and EPR spectroscopic studies as well as to photoluminescence measurement. This affords greater insight into the mechanisms of the photocatalytic reactions as we illustrate in this short review. Open-structure solids such as mesoporous silica and zeolitic aluminosilicates offer a generally applicable strategy to design new single-site photocatalysts such as those described here for the decomposition of NO₂ and O₂ and for the selective oxidation of CO in the presence of H₂.

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Single-site heterogeneous catalysts, typified by those illustrated in Fig. 1, possess numerous advantageous properties.¹ First, because of the spatial isolation of

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their active sites, they yield well-defined products (just as dispersed molecular homogeneous catalysts do) and, indeed, immobilization of many homogeneous catalysts often greatly enhances their behavior because their aptitude to undergo bimolecular deactivation is suppressed.² Second, the spatial separation of the active sites also makes it easier to



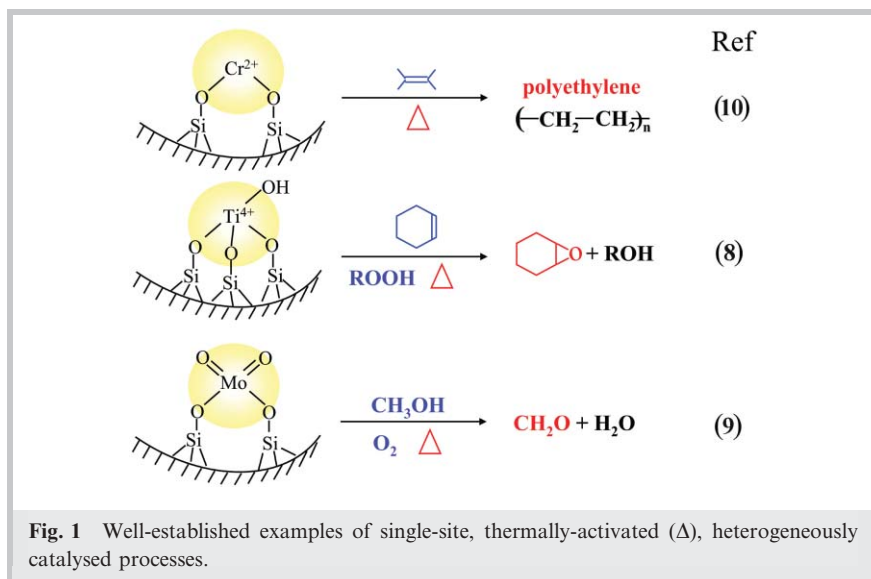
Masakazu Anpo, a full Professor of Applied Chemistry at Osaka Prefecture University, has held invited Professorships at Pierre et Marie Curie University, Paris, Torino, Shanghai, and Tokyo. In 1981 he was a Research Associate in K. U. Ingold's laboratory at the NRC, Ottawa. A pioneer in the photochemical behaviour of solid surfaces—his first book on this topic (“Photochemistry on Solid Surfaces”) appeared

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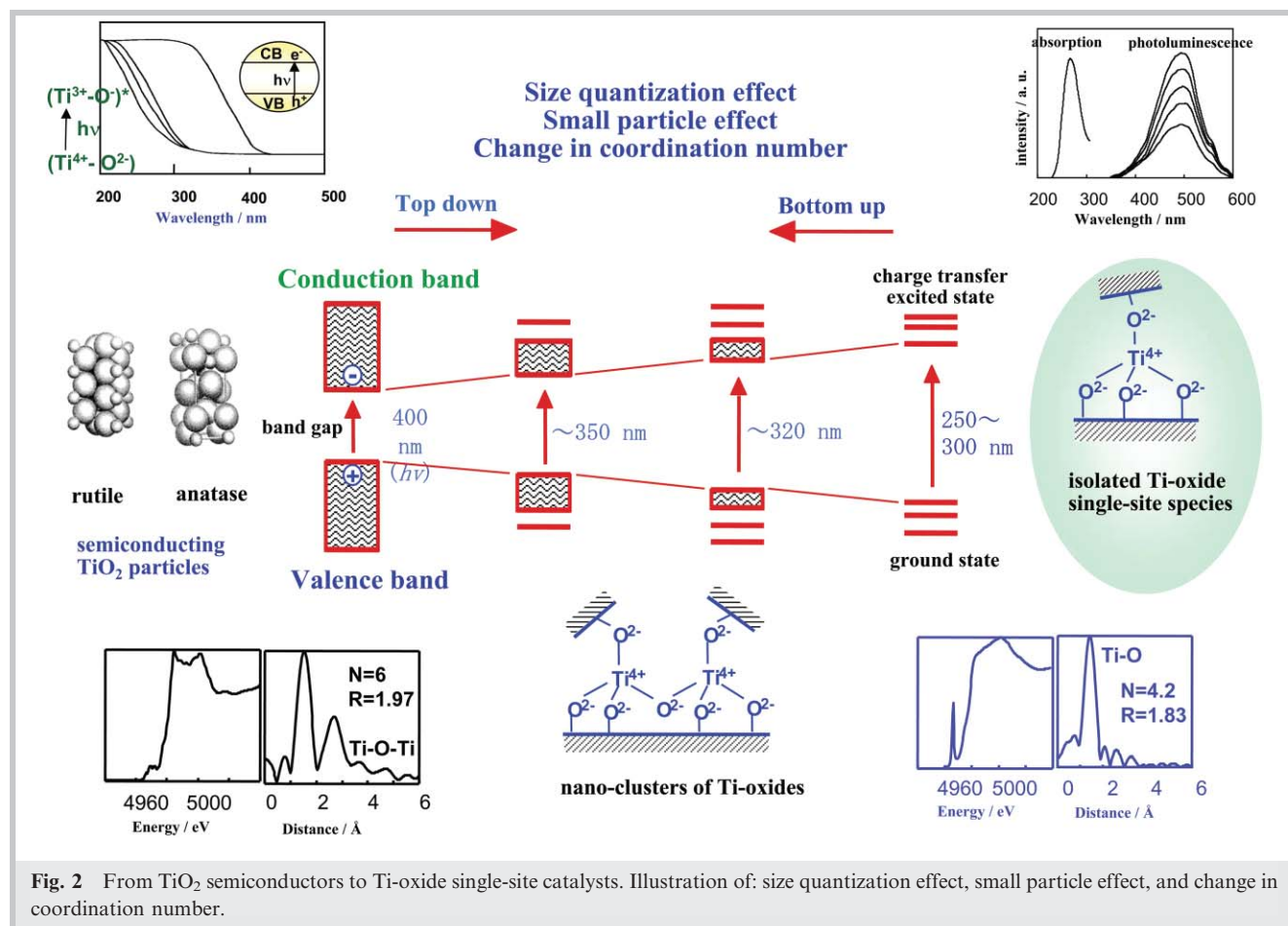


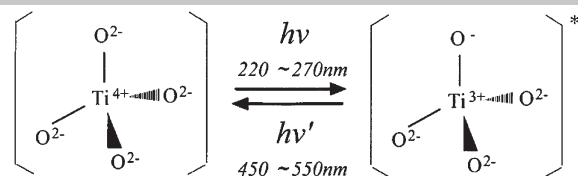
elaborated in previous work,¹ they offer a generally applicable strategy for the design of new heterogeneous catalysts involving many novel conversions and syntheses and a range of oxidations, reductions, alkylations and aminations.^{3,10,11} They also facilitate the design of bi-functional catalysts such as those that convert cyclohexanone to caprolactam by the parallel agency of redox and Brønsted acidic active site centres.¹²

Ever since Honda and Fujishima¹³ demonstrated the UV light-induced cleavage of water using a TiO_2 photoelectrode, there has been enormous interest in the use of TiO_2 and other extended oxide and chalcogenide semiconductors for the related purposes of environmental remediation, where toxic materials at low concentrations are photocatalytically converted to harmless oxidation products.¹⁴ TiO_2 as a photocatalyst has many attractive features: a convenient band gap between its valence band and conduction band of 3.0 eV (400 nm) (Fig. 2), high stability, low cost,

characterize and identify (in atomic detail) their nature and their interaction with reactants by the application of techniques such as X-ray absorption,^{3,4} fine structure (at the near edge, XANES and extended edge, EXAFS), FTIR,

UV-Vis, EPR, photoluminescence, and microcalorimetry.⁵⁻⁷ Moreover, most of these techniques may be used under conditions of catalytic turnover (*in situ*) with both liquid and gases at ambient pressure.^{3,5,7-10} Finally, as has been

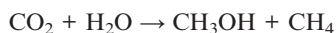
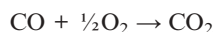
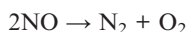




Scheme 1 The formation of charge transfer excited state with tetrahedrally coordinated titanium oxide moieties by UV light adsorption and their radiative decay process (phosphorescence).^{15,16}

non-toxicity and good performance in the oxidation of organic pollutants to CO_2 and H_2O .¹⁵

For the reactions that concern us here (see below), however, there is little merit in using the extended solid, where Ti^{4+} ions are in six-fold coordination.



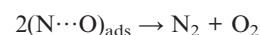
Instead it is better, as becomes clear from the arguments and examples that

follow, to capitalize on the charge-transfer excited state⁵ that forms with tetrahedrally coordinated Ti^{4+} ions when bound to oxygen (or oxygen and an OH^- group), as in Scheme 1.^{3b,16}

Precisely the same situation that applies to four-coordinated Ti^{4+} is also valid for two-coordinated Cu^+ ions when present as spatially separated entities such as extra-framework cations in zeolites of high Si : Al ratio as in ZSM-5 and Y-zeolite.

From the application of the various techniques of *in situ* characterization depicted in Fig. 3, we can deduce the reaction mechanism along with details of

the individual steps involved for the conversion of NO to its component parts:^{4,17,18} the first NO molecule forms a nitrosyl adduct at the 2-coordinated Cu^+ active site; an electron is transferred from the excited Cu^+ ($3d^9 4s^1$) state into the π -anti-bonding orbital of NO, and this is followed by the donation of an electron from another NO molecule into the Cu^+ , thereby yielding two contiguous ($\text{N}\cdots\text{O}$) species adsorbed to the active centre. Liberation of the two gases occurs when these contiguous species combine:



It is to be noted that the 2-fold coordination of Cu^+ along with the Cu–O bond distance of the initial active site, as well as the FTIR and EPR fingerprints of the nitrosyl adducts are determined by *in situ* experiments. It is also seen that $\text{Cu}^+/\text{ZSM-5}$ is significantly better than $\text{Cu}^+/\text{Y-zeolite}$ as a photocatalyst, a fact that could arise from the greater polarizing electrostatic field at the Cu^+ ions in the narrower pore ZSM-5.^{17,18}

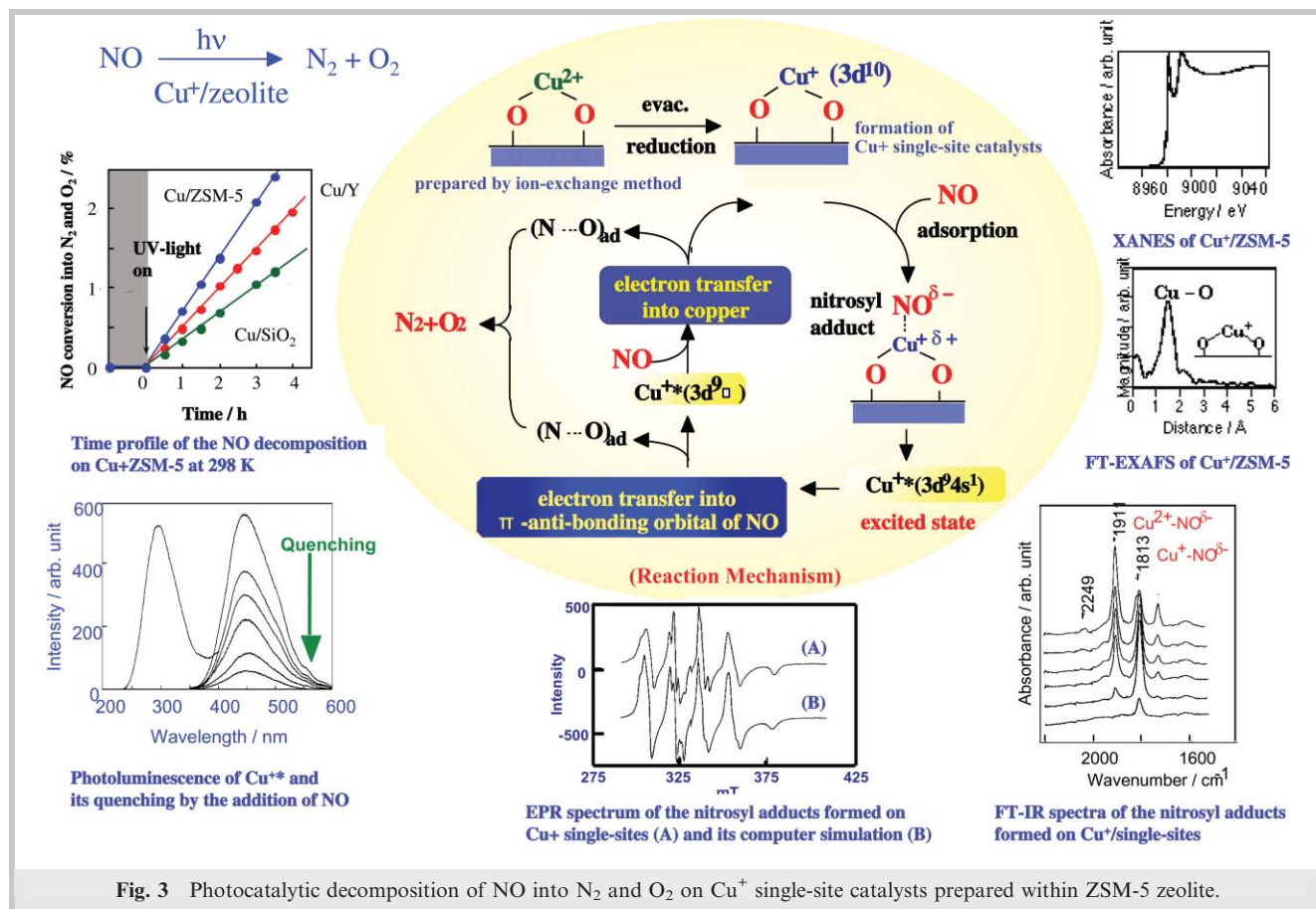


Fig. 3 Photocatalytic decomposition of NO into N_2 and O_2 on Cu^+ single-site catalysts prepared within ZSM-5 zeolite.

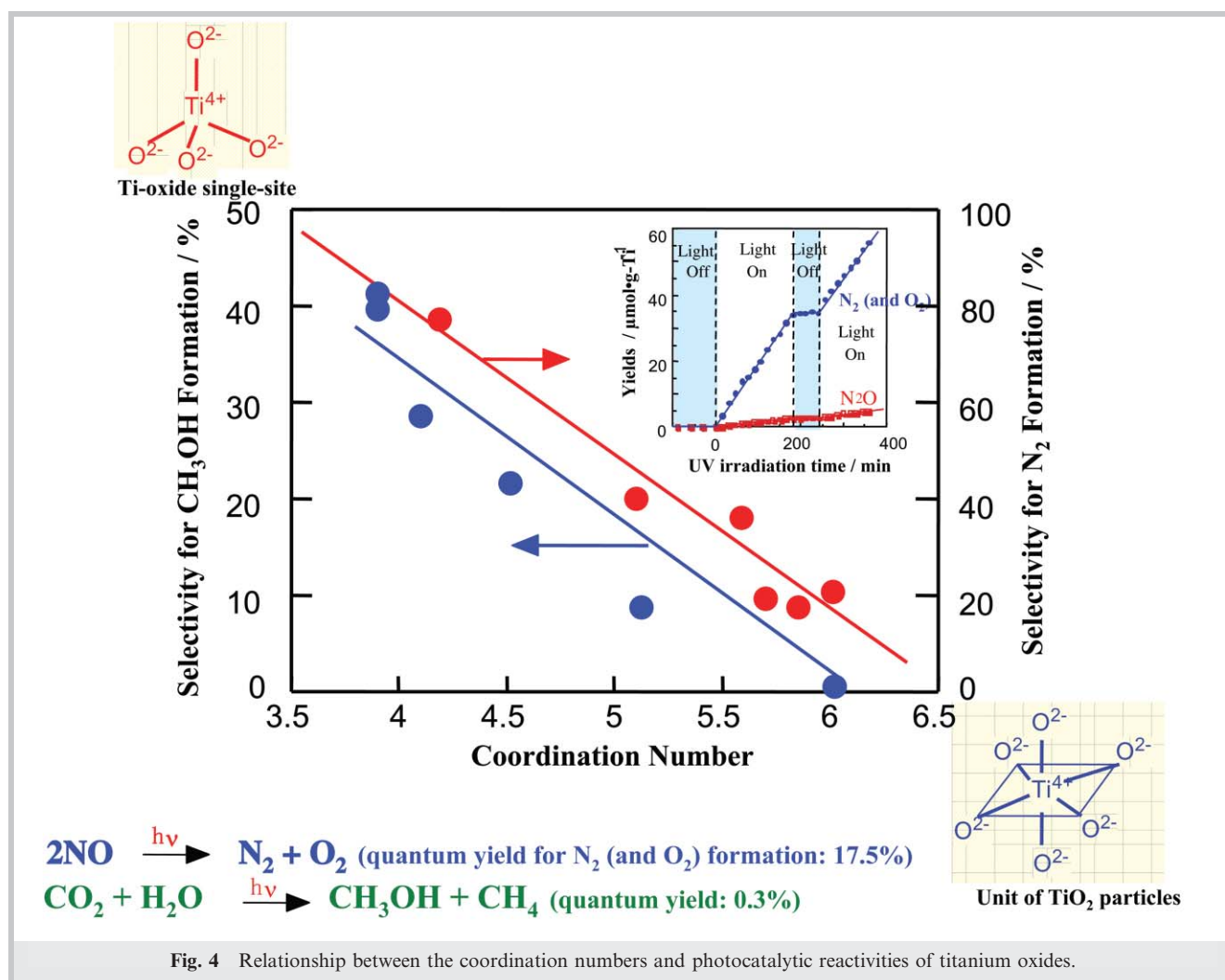


Fig. 4 Relationship between the coordination numbers and photocatalytic reactivities of titanium oxides.

Reverting to the single-site Ti^{4+} oxo-centered catalyst (Fig. 4), it is seen that its performance both in the decomposition of NO and in the reduction of CO_2 with H_2O improves the more spatially separated the Ti^{4+} oxo ions are and the lower their degree of coordination, which facilitates the formation (compare with Fig. 1) of the charge-transfer localized excited state.^{19,20} It is not unexpected that the quantum yield of the $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_4$ reaction is substantially smaller than that of the decomposition of NO, as the former process requires a more demanding configuration of co-adsorbed reactants involving six participating atoms.

So far as the photo-oxidation of CO by O_2 is concerned—an important reaction in fuel cell technology²¹ since it is essential to remove CO impurities from H_2 otherwise electrode performance is

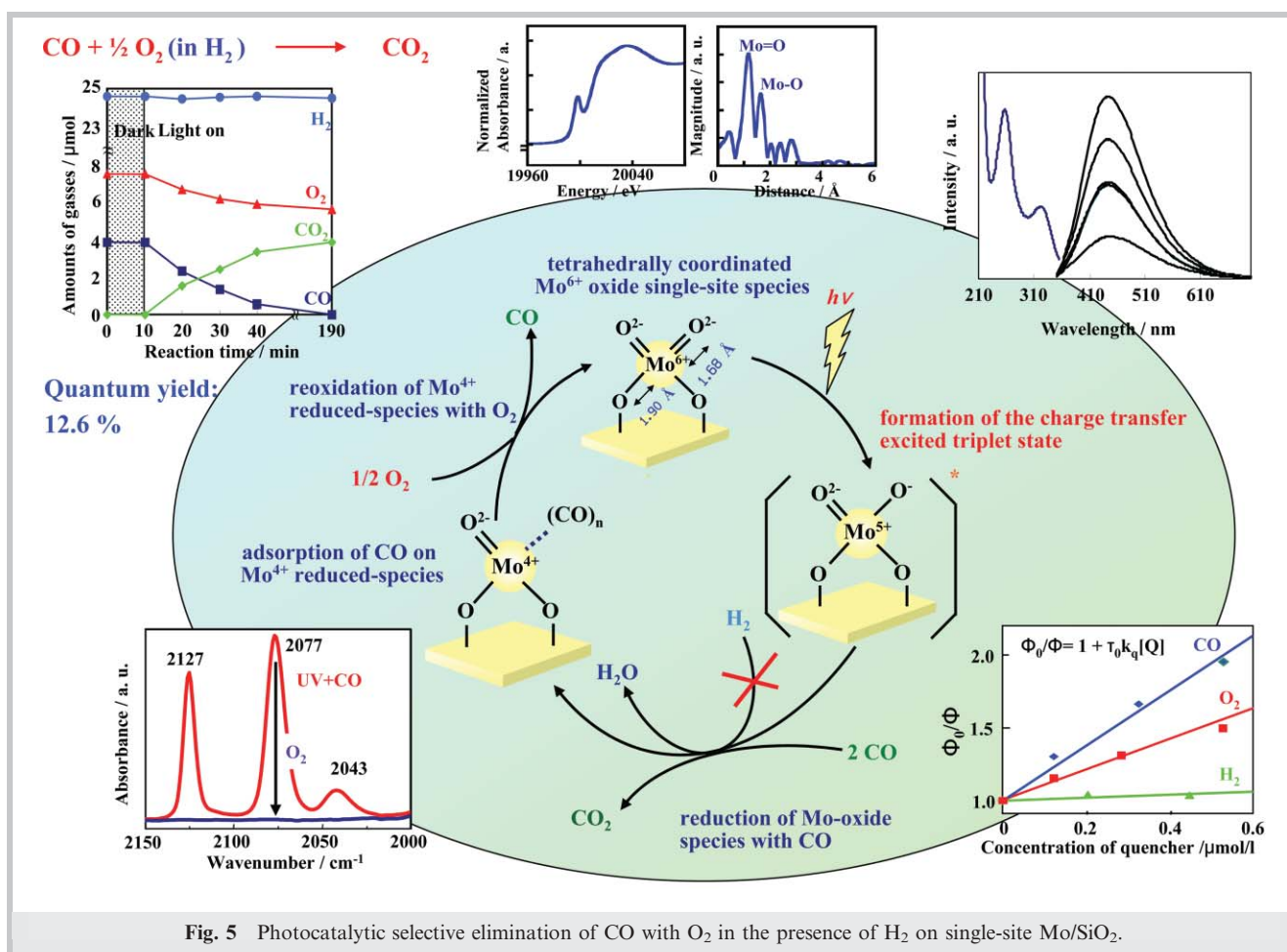
poisoned—we are again led to a plausible mechanism (Fig. 5) based on the known structures, as determined by XAFS, of the single-site Mo^{6+}O_4 centre.²² Again a charge-transfer excited triplet state is implicated (and observed), and good quantum yields are obtained. This single-site photocatalytic method of purifying H_2 from its unwanted CO impurity is an alternative to the thermally-activated heterogeneous catalytic method of achieving the same end using a Pt–Fe and other noble-metal catalysts supported on alumina.²¹

The advantages of single-site solid catalysts seen here in the context of harnessing solar energy are already well-recognized in many thermally-activated processes, including both those of prime industrial or commercial value such as the wide range of selective oxidations using either H_2O_2 ²³ as a liquid oxidant or acetyl peroxyborate as a solid

oxidant²⁴ and others of currently mainly academic interest.²⁵

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