Photoinduced Processes in Heterogeneous Gas-Solid Systems. Temperature Dependence and Modeling of a Surface Chemical Reaction on ZrO_2 Triggering Photophysical Events in the Solid

A. Emeline,[1] S. Polikhova,[2] V. Ryabchuk,[2] N. Serpone[1,3]
[1] Department of Chemistry & Biochemistry, Concordia University, Montreal (QC), Canada H3G 1M8.
[2] Department of Physics, University of St. Petersburg, St. Petersburg 198504, Russia.
[3] Dipartimento di Chimica Organica, Universita di Pavia, Pavia, Italia

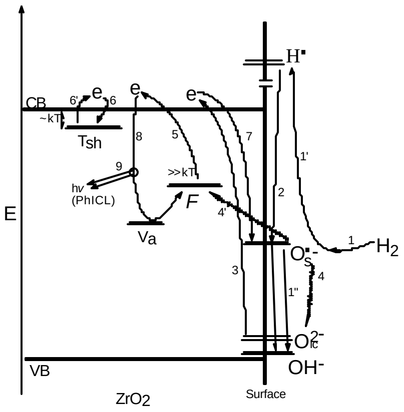
Chemisorption of H-containing molecules, e.g. H_2, H_2O, RH and ROH, on pre-irradiated metal-oxide surfaces emit light following interaction of these molecules with photogenerated surface-active centers. Earlier we showed that this effect is also typical for adsorption of H_2 on pre-irradiated powdered ZrO_2 (1,2). The light pulse from the PhICL effect follows bi-exponential decay kinetics with the longer component corresponding to the decay of phosphorescence. PhICL emits photons in a broad spectral range with the maximum at ca. 490 nm. The PhICL spectrum corresponds to the spectra of phosphorescence and thermo-stimulated luminescence (TSL) of ZrO_2. This infers similar mechanisms of the emission process, namely trapping of electrons by deep traps such as anion vacancies, V_a. This PhICl effect is another example of the interconnection between chemical and physical relaxation pathways in heterogeneous systems.

We describe the results of extended experimental studies of the PhICL effect caused by adsorption of H_2 on a pre-irradiated surface of ZrO_2. The data are compared with processes of adsorption of another H-containing molecule, namely CH_4. In particular, we examine the results when the chemical reaction between H_2 (or CH_4) and the surface of ZrO_2 nanoparticles occurs (a chemical relaxation pathway) after the solid had been pre-irradiated (*in vacuo* or O_2) and the intrinsic phosphorescence from zirconia had terminated. Introduction of H_2 triggers physical relaxation processes, which are manifested as an after-glow (i.e. a PhICL light pulse) in heterogeneous gas-solid systems (1-3). Unlike H_2, CH_4 does not yield a detectable PhICL emission. The reactions were examined in the temperature range 75 K to 600 K.

For a non pre-irradiated surface, the H-containing molecules physisorb with binding energies E_{phys} = 33 kJ mol^{-1} (0.34 eV) for H_2 and 52 kJ mol^{-1} (0.54 eV) for CH_4. Subsequent to pre-irradiation of ZrO_2, the molecules chemisorb dissociatively to yield appropriate free radicals (H• for H_2, and CH_3• for methane – the other H• is trapped) through an activated process. The relevant activation energies are E_a = 30 kJ mol^{-1} (0.31 eV) for H_2 and E_a = 32 kJ mol^{-1} (0.33 eV) for CH_4 if the process occurs by a Langmuir-type pathway. If the process takes place by an Eley-Rideal mechanism, the relevant E_as are 41 kJ mol^{-1} (0.43 eV) for H_2 and 46 kJ mol^{-1} (0.48 eV) for CH_4.

The results were modeled using a sequence of differential equations that considered (a) only generated electrons from interactions of H• atoms with surface O^{2-} anions {H• + O^{2-} ö OH^- + e}, (b) the possibility that O_s^-• active centers physically decay through recombination with free electrons {e + O_S^-• ö V_C}, (c) a chemical reaction between H• atoms with O_S^-• surface active centers (H• + O_S^-• ö OH^-}, and (d) recombination of free electrons with O_s^-• active centers {e + O_S^-• ö O^{2-}}. A mechanism is proposed in which surface chemical reactions cause the release of the energy stored during the pre-irradiation stage of the solid. This leads to photoinduced formation of metastable defects in the solid (e.g., O_S^-•), together with deep electron traps (***F*** centers) that lead to both chemical and physical relaxation of the system. The latter is manifested as a PhICL emission triggered by the adsorption of such donor molecules as H_2. As a result of this spontaneous process, the pre-photoexcited system returns to its lower energy state.

Some conclusions can be reached regarding some of the steps in the PhICL process, even with our present level of understanding (see mechanism in the Scheme). Photoexcitation of a solid (e.g., zirconia) at the appropriate energy leads to light energy conversion and storage by the photogeneration of defects in the solid (e.g., ***F*** color centers, O_S^-•, and others). In addition, the surface states themselves (e.g., $O^{2-}{}_{lc}$) are significant defects with respect to the solid bulk. They are poised to participate in relaxation processes.



Scheme

Step 1 in the Scheme represents dissociative chemisorption of H_2 molecules on photogenerated surface-active hole centers, which leads, in part, to the relaxed state of the surface OH^- group (step 1") and to the formation of highly energetic H• atoms (step 1'). Step 2 describes the chemical reactions of atomic hydrogen with the surface defects O_S^-• and/or $O^{2-}{}_{lc}$ yielding a chemical pathway for the system to relax. This is subsequently accompanied by the release of energy (step 4) and/or by the generation of free electrons (step 3), which trigger the physical pathway of system relaxation. Energy transfer to the solid electronic subsystem (step 4') also leads to the generation of free electrons (step 5) by detrapping from deep energy ***F*** centers. The physical relaxation processes in the solid, for example trapping by and detrapping from the shallow traps (steps 6 and 6'), determine the fate of these electrons. The latter steps 6 and 6' are those that are responsible for the temperature dependencies of the PhICL emission, as well as for the recombination with hole states on the surface (step 7) and in the bulk (not shown), and for the trapping by deep energy electrons traps (step 8) to induce the PhICL emission (step 9).

References

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