

NOTE

Catalyst Deactivation in Gas–Solid Photocatalysis

Photocatalyst lifetime is potentially important in process economics, as it sets maximum run times between catalyst regeneration or replacement. This note surveys the literature of photocatalytic air treatment and purification in order to identify the emerging photocatalyst deactivation issue. For each pertinent paper, we (1) evaluate the total number of molecules converted by a photocatalyst over time and (2) compare this cumulative photocatalytic molecular conversion to the estimated total number of illuminated surface sites. This comparison establishes that photocatalyst deactivation is virtually always found in single-pass fixed-bed photoreactors for cumulative contaminant conversions in excess of 1–10 equivalent monolayers.

Deactivation of heterogeneous thermal catalysts has been extensively studied for commercial thermal catalytic processes and is well reviewed elsewhere [1–8]. There are appreciable difficulties associated with obtaining catalyst deactivation data, for which Butt and Peterson [3] indicate that “the ideal reactor system would be one in which the concentrations in the reaction mixture and the temperature remain constant throughout the deactivation period,” as could be achieved with a differential conversion reactor with a partial recycle stream. Their modeling showed that expected performance of a fixed-bed reactor is more sensitive to catalyst deactivation than is a fluidized or moving-bed reactor. The fixed-bed reactor we expect, therefore, to be the most sensitive configuration for detecting deactivation.

During butanol photooxidation, Blake and Griffin [9] identified a surface-adsorbed carboxylate species which they suggested could accumulate on the surface and block catalyst sites. Cunningham and Hodnett [10] earlier observed, during propan-2-ol oxidation, a decay in catalyst activity for ZnO and TiO₂ photocatalysts. Larson and Falconer [11] carried out trichloroethylene (TCE) destruction in air and used temperature-programmed desorption (TPD) from fresh, used, and deactivated photocatalysts to identify adsorbed and possibly inhibitory species. Increased amounts of total adsorbed CO and CO₂ were present on the surface of the used (359 μmol/gTiO₂) and deactivated (910 μmol/gTiO₂) catalysts vs a fresh catalyst (56 μmol/gTiO₂). We estimate that ≈1.7–3.1 monolayer equivalents of CO and CO₂, combined, were recovered from their deactivated catalyst, suggesting that the entire photocatalyst surface may have been active (i.e., each TiO₂ ad-

sorption site may also have been an active catalytic site). Peral and Ollis [12] reported photocatalyst activity to decline over time for air feeds containing N or Si heteroatom contaminants: decamethyltetrasiloxane (DMTS), pyrrole, and indole. Sauer *et al.* [13] noted catalyst deactivation for a toluene/perchloroethylene (PCE) feed mixture in air in the same single pass powder bed reactor used by Peral [12].

Absence of photocatalyst deactivation during gas–solid studies has also been noted [14–18]; however, the contaminants were usually present in trace quantities and (a) were photooxidized for only a short time period in a single-pass reactor, or (b) were reacted in a batch photoreactor. The first circumstance may not generate sufficient catalyst poisoning to be detected, and the changing concentrations characteristic of batch operation could mask any relatively slower catalyst deactivation.

Catalyst lifetime or deactivation comparisons among different contaminants and laboratories need to be made on a common basis. We normalize all reports by calculating the cumulative reactant conversion in units of illuminated (active) catalyst surface monolayer equivalents (meq), defined as

$$\text{meq} \equiv \frac{\text{molecules converted}}{\text{(active) catalyst sites}} \quad (1)$$

The meq calculation requires knowledge of both the total molecules of reactant converted and the number of active (illuminated) catalyst sites. These quantities are not normally reported; we calculated or estimated them from data in references cited. Molecules converted are calculated given the reactant feed concentration, volumetric flowrate, conversion, and the total reaction time. The number of active catalyst sites is unknown, so we repeat an approach used previously in liquid–solid photocatalysis [19] and adopt the catalyst surface site density of 5×10^{14} sites/cm² as a basis. We recall that the TPD data of Larson and Falconer [11] suggest that the entire surface may be photoactive, in as much as a fully deactivated photocatalyst was found to desorb in excess of an apparent monolayer equivalent of CO and CO₂. The total number of assumed active sites can then be calculated for any prior report by knowing the photoreactor geometry, catalyst-specific surface area (m²/g), and the penetration depth of illumination (see the sample calculation in the appendix of [20]).

TABLE 1
Data Summary for Gas-Solid Studies from Which Surface Monolayer Equivalent (meq) Were Calculated

Reference	Reactant ^a	Median active surface area (m ²)	All catalyst illuminated?	Feed concentration range (mg/m ³)	Feed flowrate range (cm ³ /min)	Reaction time range (hrs)	Fractional conversion range	Meq range (molecules/site)	Deactivation reported?	Reactor type: SP = single pass B = batch
(14)	TCE	50	N	13200	80-650	100	0.61-0.94	70-884	Y	SP
(13)	TCP ^b	0.037	N	219-333	1.0	7	0.1-1.0	17-595	Y	SP
(13)	PCE ^c	0.037	N	740	1.0	7	0-0.8	46-85	Y	SP
(13)	T ^b	0.037	N	10-43	1.0	7	0.1-1.0	4.9-61	Y	SP
(13)	T ^c	0.037	N	20.3-40.0	1.0	7	0-1.0	14.24	Y	SP
(12)	P	0.037	Y	205	50	47	0-0.61	37-144	Y	SP
(12)	DMT	0.037	Y	210	50	100	0-0.43	141	Y	SP
(12)	I	0.037	Y	58	50	54	0-0.79	23-120	Y	SP
(12)	DMS	0.037	Y	100	50	25	0.05-0.1	26	N	SP
(22)	B	0.037	N	260	70-120	8.3	0.12-1.0	10.4-110	Y	SP
(21)	MB	0.56	N	34500	40	0.5	0.4	40.4	N	SP
(24)	TCE	3.8	N	8-79	261-319	0.5-4.6	0.5-1.0	0.09-2.4	Y	SP
(11)	TCE	?	?	?	?	?	?	0.13-2.2	Y	SP
(25)	TCE	99	?	600	300	0.13	0.99	0.013	N	SP
(26)	T	41.6	?	100	300	.2	0.63	0.0025	N	SP
(27)	E ^d	0.105	Y	90-400	93000	2.0	1.0	197	N	B
(27)	Ac ^d	0.105	Y	80-330	93000	2.0	1.0	165	N	B
(27)	E ^e	5.23	N	65-370	93000	13	1.0	19.8	N	B
(27)	Ac ^e	5.23	N	140-420	93000	7	1.0	6.2	N	B
(20)	A	5.23	N	70-400	93000	7	1.0	7.8	N	B
(28)	T	250	N	97	5000	1.0	1.0	0.01	N	B
(28)	Ac	250	N	26	5000	1.0	1.0	0.006	N	B

^a B = 1-butanol; DMT = decamethyltetrasiloxane; P = pyrrole; I = indole; DMS = dimethyl sulfide; A = acetone; T = toluene; MB = methyl butanol; Ac = acetaldehyde; and E = ethanol.

^b Toluene/trichloropropene (TCP) mixed feed.

^c Toluene/PCE mixed feed.

^d Glass reactor.

^e Monolith reactor.

Table 1 summarizes data from gas-solid photocatalysis publications for which we could calculate or estimate the illuminated solid surface area. These data include active (illuminated) catalyst surface area, contaminant feed conditions (flow rate and concentration), reaction time, and the fractional conversion range used to estimate the total meq's converted. Also listed are the reactor type used (recycle batch (B) or single-pass (SP) fixed-bed) and whether catalyst deactivation was reported (yes (Y) or no (N)) for each study. This list does not include reports where the meq converted could not be calculated, due to either the lack of necessary information or to results which were not easily interpreted. The tabulated cumulative conversions cover a wide range of monolayer equivalent values (0.0025-884 meq); catalyst deactivation was mentioned in half these studies. None of the *batch* reactor studies, regardless of the meq value obtained, reported catalyst deactivation. This result is plausible, as all batch concentrations change with time, a circumstance that could easily mask any slow deactivation. In the batch reactors, deactivation would only be clearly evident if repeat runs were made without catalyst pretreatment or regeneration between runs; such repeat run data

are non-existent in the photocatalyst gas-solid literature as of this date.

For *single-pass fixed beds*, the calculated meq's are listed in increasing order in Fig. 1. Deactivation was reported (or noted) for 12 of the 13 reactor studies which achieved contaminant conversions of at least 1.0 meq, whereas results limited to maximum conversions well below 1.0 meq did not report catalyst deactivation. This common detection of catalyst deactivation in single-pass fixed-bed studies is not surprising, as we recall that this catalyst configuration and operating mode is most adversely affected by deactivation [3].

The single, early fixed-bed flow study that did not show catalyst deactivation involved photooxidation of methylbutanols [21]. Catalyst deactivation with trace-alcohol feeds to fixed-bed photocatalytic reactors has since been reported elsewhere for both butanol [9, 10, 22] and isopropanol [10, 23].

Further catalyst deactivation (and regeneration) studies in gas-solid photocatalysis are evidently necessary to establish clearly the process economics of this technology. The type of fixed-bed photocatalytic reactor chosen to detect

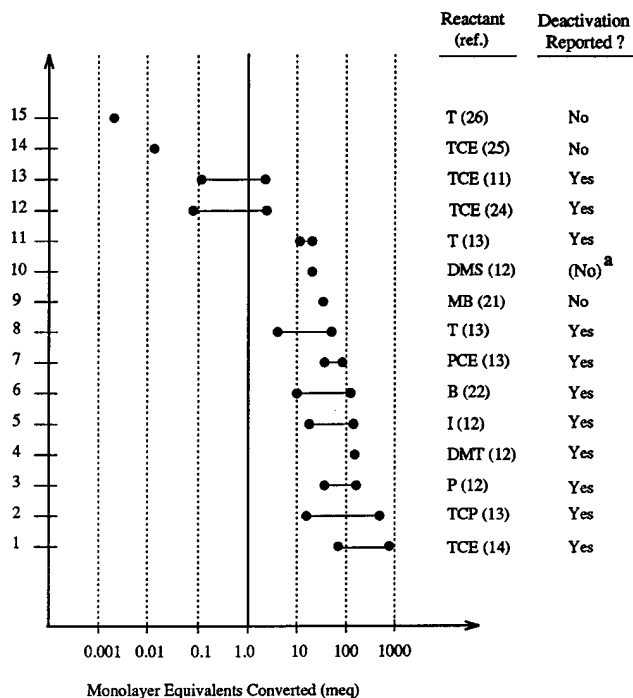


FIG. 1. Literature summary: monolayer equivalents converted for single-pass fixed bed reactors (FB) (ordered in increasing (meq) values). ^adenotes that deactivation was not reported, but was evident upon review of the data.

and measure deactivation phenomena is shown here to be important: single-pass flow reactors are more sensitive than batch recycle reactors.

Questions for future studies include: Why is deactivation so common in gas–solid photocatalytic reactors, what are the underlying mechanisms, and how can these deactivations be avoided or be offset by periodic regeneration?

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