

## Effect of mass transfer limitation on catalytic activity and selectivity for oxidation of glycerol

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### Highlights

- The effect of mass transfer limitation has been studied for glycerol oxidation
- Observed difference in product selectivity in mass transfer limited zone compare to kinetic regime
- Trend of product selectivity are complex because of involvement of both i.e. solution and catalyst surface mediated steps.

### 1. Introduction

Glycerol oxidation proceeds by a complex mechanism with multiple side reactions that hamper the selectivity towards the desired (C<sub>3</sub>) product(s). The multiphase (gas-liquid-solid) character of the system poses further challenges to reaction engineers. Attempts to improve selectivity over the past two decades have focused mainly on improved catalysts, but claims on such catalysts are often backed by a clear demonstration of an absence of all transport limitations in the study. The reactor performance, activity and selectivity depend not only on intrinsic kinetics but also on transport rates (internal and/or external) in general, which govern oxygen and glycerol mass transfer to the catalytic site. Very few groups [1] have actually attempted to ensure kinetic control before studying the kinetics and influence of different parameters, such as pH, temperature, pressure, and catalyst loading. With this background, this study focuses on mass-transfer limitations (both internal as well as external) in batch studies, and delineate the influence of such limitations on selectivity and activity of catalysts in industrial flow reactors.

### 2. Methods

For mass-transfer studies, mainly, three catalysts - Pd/AC, Au/AC-TiO<sub>2</sub> and Pd/SiO<sub>2</sub> were used. Pd/AC and Au/AC-TiO<sub>2</sub> were obtained from Merck (India) and Premier Catalyst (USA), respectively and Pd/SiO<sub>2</sub> was obtained from the Vineeth chemicals (India). Details of experimental methodology and product analysis may be found elsewhere [2].

The Catalysts were characterized using techniques such as TEM, BET and pulse chemisorption. Hydrogen was used as the pulse gas in the case of gold catalyst, while CO was used in the other cases. The BET surface area was found to be 250 m<sup>2</sup>/g, 1500 m<sup>2</sup>/g and 1200 m<sup>2</sup>/g for Pd/SiO<sub>2</sub>, Pd/AC and Au/AC-TiO<sub>2</sub>, respectively. TEM analysis showed that the average particle diameter of the metal, in both Pd-based and Au-based catalysts was between 5 nm and 8 nm.

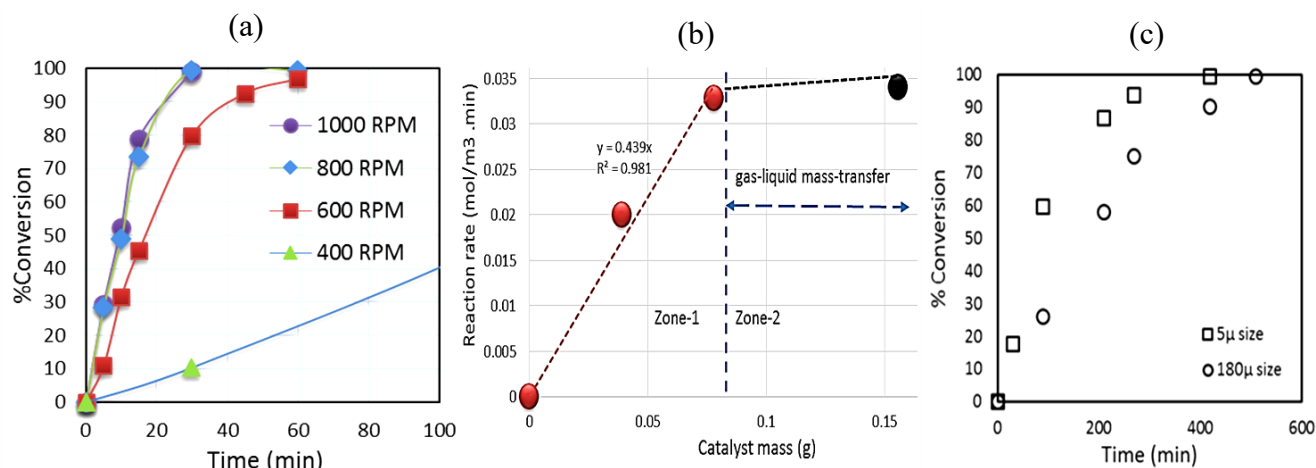
#### *External mass transfer studies*

Experiments performed with different catalyst loading, and at different RPM, were used to estimate the influence of gas-liquid mass transfer. The most common test to verify if mass transfer (through a liquid-solid interface) controls a catalytic reaction in a batch reactor is to look for an influence of the agitation rate (RPM) [3].

#### *Internal mass transfer studies*

To investigate internal mass-transfer, the performance of catalyst particles of different sizes was evaluated under conditions free of external mass-transfer limitations. By reducing the particle size, a point is reached such that a further decrease does not change the reaction rate. These studies were also supplemented using the W-P (Weisz-Prater) criterion [4] to check for the effect of pore-diffusion, if any.

### 3. Results and discussion



**Figure 1.** (a) Glycerol conversion as a function of time showing presence of external mass transfer limitations at low RPMs (Pd/C catalyst) (b) Volumetric reaction rate as a function of catalysts loading (Pd/AC) and (c) absence of internal mass transfer limitation for smaller size catalysts (For Pd/SiO<sub>2</sub>).

Fig. 1(a) shows the effect of RPM on the observed reaction rate for Pd/C, at a catalyst loading of 0.078g. It is seen that the rate is insensitive to RPM above 800 RPM. Figure 1(b) shows the effect of catalyst loading on the observed reaction rate, at an RPM of 800. It is seen that, under these agitation conditions, the gas-liquid mass transfer (MT) resistance does not play a significant role at catalyst loadings up to 0.078g (Glycerol/metal ratio=1000 mol/mol). Detailed product concentration profiles however show that the selectivity to glyceric acid is higher under conditions of mass transfer limitations (for both the studied catalysts i.e. Pd/AC and Au/C-TiO<sub>2</sub>). Furthermore, reaction with varying particle sizes shows an effect of internal MT on catalyst activity (Fig 1(c)) and the selectivity. Influence of internal pore diffusion on catalytic process were evaluated by the Weisz-Prater criterion with certain assumptions (1<sup>st</sup> order reaction, for strong diffusion limitation over spherical particle), details can be found elsewhere [2]. It was found that WP criterion with respect to both the reactants - glycerol and oxygen, was well below 0.3 for 5 micron catalysts size while 180 micron catalyst shows internal diffusion limitations.

### 4. Conclusions

Glycerol oxidation being a combination of complex series-parallel reaction, occurs over catalyst surface i.e. solid phase as well as in the solution phase. The influence of transport limitations suggest that the trends of product selectivity are likely to be complex because of the involvement of solution-mediated reactions in addition to reactions on the catalyst surface.

### References

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### Keywords

Mass transfer limitations, Glycerol oxidation, Weisz-Prater criterion, Pore diffusion