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Agglomeration and adhesion of catalyst particles in gas–liquid reactors

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Abstract

The colloidal properties of catalysts present in three phase slurry reactors may affect the overall behaviour of such a reactor. In part, this may arise from the adhesion of such particles to gas bubbles, which may lead to enhancement of the G–L mass transfer [Catal. Today 48 (1999) 131]. Classical film theory based on the mass transfer models are capable of quantitatively predicting such mass transfer enhancement, but only on the basis of a priori knowledge of the degree of bubble coverage by particles. Presently, various methods are reviewed that allow the accurate experimental determination of the coverage of bubbles by particles, under both stagnant and non-stagnant conditions. The relevance of these phenomena to reactive systems will be demonstrated on the basis of mass transfer data for the hydrogenation of methyl acrylate in a slurry reactor.

Keywords: Hydrophobic; Carbon; Colloidal properties; Slurry reactors; Flotation

1. Introduction

Three-phase slurry reactors are widely used in chemical and biochemical industries. In most of these reactors, a catalyst is present as a dispersed solid phase. The impact of the presence of such particles on the hydrodynamics of a three-phase slurry reactor, be it on the G–L mass transfer rate or on the coalescence of bubbles, is subject of debate. Hydrophobic catalyst particles present in an aqueous liquid phase may either agglomerate or adhere to gas bubbles. The latter may give rise to increased G–L mass transfer rates and may thus enhance conversion rates in a three-phase reactor [1]. Vinke et al. [2], using bubble-pick-up experiments, showed that under stagnant conditions small hydrophobic particles may adhere to bubbles in aqueous slurries, while hydrophilic particles do not.

In earlier work, a model was formulated to describe mass transfer enhancement under reaction conditions [1], employing the bubble coverage ζ as input parameter. In order to study adhesion of particles to bubbles, an accurate method to measure the bubble coverage is required. To this end, we used both bubble-pick-up experiments [2] and flotation experiments to assess adhesion under stagnant and non-stagnant conditions, respectively. Flotation is studied using the so-called Hallimond tube, which is often used in laboratory-scale flotation experiments [3]. The mass transfer model developed earlier was verified by studying the hydrogenation of methyl acrylate in water, using Pd-on-carbon as a hydrophobic catalyst and Pd-on-alumina as inert, that is non-adhering, catalyst. By choosing appropriate reaction conditions, it was asserted that for both catalysts the reaction was fully G–L mass transfer controlled. Thus, during reaction

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adhesion can be studied through its impact on mass transfer rates.

Nomenclature

d_b	bubble diameter (m)
d_p	particle diameter (m)
E	enhancement factor (–)
P_a	adhesion probability (–)
P_c	collision probability (–)
P_d	detachment probability (–)
P_f	flotation probability (–)
Re	Reynolds number based on the bubble size, $\rho u_b d_b/\eta$ (–)
t_i	induction time (s)
u_b	bubble velocity ($m\,s^{-1}$)
Greek symbols	
α	bubble coverage angle (°)
γ_s	catalyst concentration ($kg\,m^{-3)}$
ε	void fraction (–)
ζ	bubble coverage (–)
η	viscosity (Pa s)
θ	three-phase contact angle (rad)
ρ	liquid density ($kg\,m^{-3}$)
ρ_{pg}	density of particles, pores filled with gas ($kg\,m^{-3}$)
σ_{LV}	liquid–vapour surface tension ($N\,m^{-1}$)

2. Theory

To study the particle-to-bubble adhesion and agglomeration of catalyst particles, experiments were carried out under stagnant and non-stagnant conditions. The non-stagnant experiments described refer to the flotation experiments in a modified Hallimond tube.

During flotation, the particle-to-bubble flotation probability is an important parameter. This probability P_f is a function of the hydrodynamic conditions in the column, and can be described by the following equation [4]:

$$P_f = P_c P_a (1 - P_d) \tag{1}$$

The adhesion probability P_a is a function of the three-phase contact angle θ, the particle diameter, and the bubble diameter. For particles smaller than 100 μm, the detachment probability P_d is negligible [4]. The collision probability P_c is mainly determined by the hydrodynamics in the reactor. The adhesion probability and collision probability for laminar conditions is given by Eqs. (2) and (3) [4]. The Reynolds number used in this equation is based on the bubble diameter. For laminar flow conditions, as prevailed in the Hallimond tube, the adhesion probability is a function of the particle diameter. This is not the case for turbulent conditions, as prevailed in the stirred reactors.

$$P_a = \sin^2\left[2 \arctan \exp\left(\frac{-((45 + 8\,\mathrm{Re}^{0.72})u_b t_i)}{15 d_b (d_b/d_p + 1)}\right)\right] \tag{2}$$

$$P_c = \left[\frac{3}{2} + \frac{4\,\mathrm{Re}^{0.72}}{15}\right]\left(\frac{d_p}{d_b}\right)^2 \tag{3}$$

The induction time t_i in Eq. (2) represents the time needed to pass the film between particle and bubble, before adhesion can occur [5]. This parameter is a function of the three-phase contact angle: a higher contact angle will result in a decreasing induction time.

In order to obtain a high collision probability, thus approaching in that respect the conditions prevailing for adhesion under turbulent conditions, the flotation column needs to be operated in such way so that a maximum particle-to-bubble collision probability is reached for all particle sizes. The flotation probability as a function of particle size for laminar flow condi-

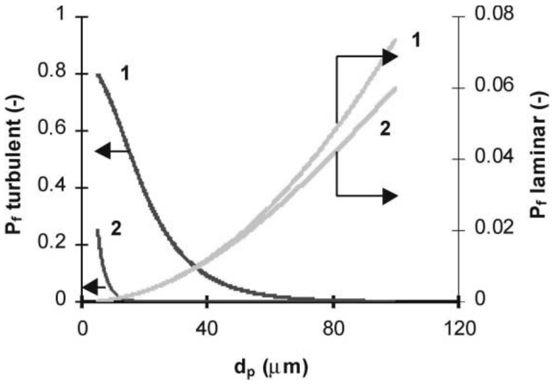

Fig. 1. Flotation probability as a function of the particle diameter for laminar (—, $P_f = P_c P_a$) or turbulent (—, $P_f = P_c P_a$) conditions in a stirred reactor. d_b = 1 mm, $\rho = 1000\,kg\,m^{-3}$, $\eta = 1 \times 10^{-3}$ Pa s. For laminar flow conditions $u_b = 0.1\,m\,s^{-1}$, for turbulent flow conditions $u_b = 1\,m\,s^{-1}$. **1**: induction time $t_i = 0.001$ s, **2**: induction time $t_i = 0.005$ s.

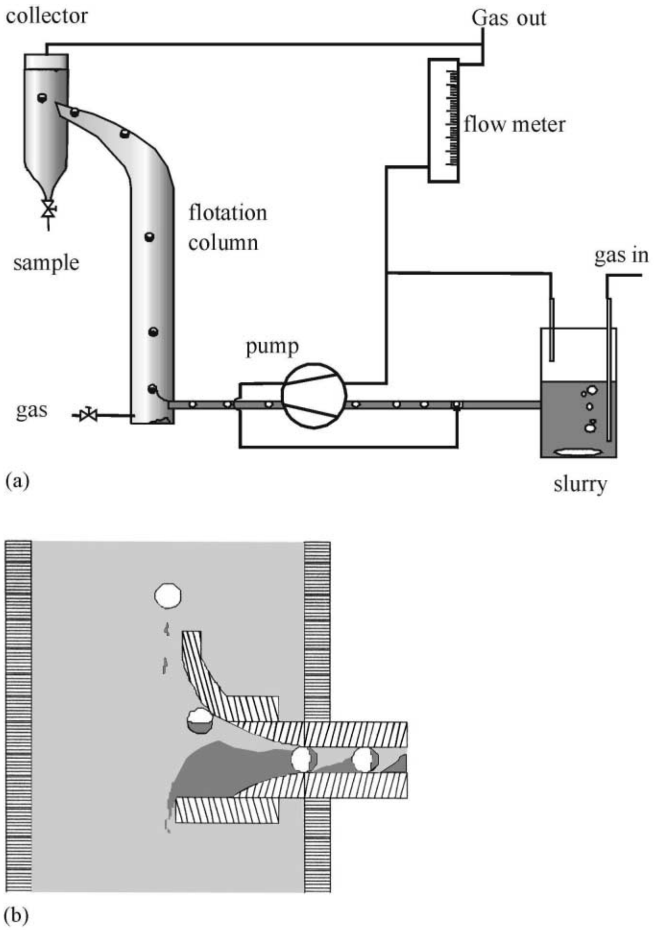

Fig. 2. (a) Schematic representation of the flotation column. (b) Schematic representation of the inlet of the flotation column.

tions and turbulent flow conditions in a stirred tank reactor at different induction times is given in Fig. 1. This figure shows that an increase in three-phase contact angle for a decreased induction time results in an increased flotation probability. Also, it shows that under laminar flow conditions, the flotation probability for small particles is about zero. This is mainly due to the low collision probability of small particles. This also explains why Roizard et al. [6] did not observe any adhesion of carbon particles under laminar flow conditions. In view of the above, a modified Hallimond tube (Fig. 2) was developed. Before bubbles enter the column, they are forced through a slurry of particles, see Fig. 3. In this way the collision probability is unity for all particles present, so only the adhe-

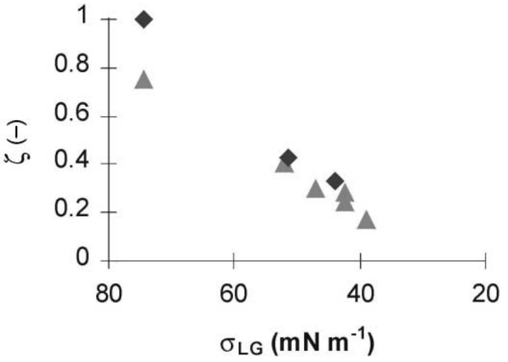

Fig. 3. Bubble coverage as a function of surface tension. The results of BPU of SX1G with N_2 (▲) and H_2 (◆).

sion probability as a result of hydrophobicity and the particle diameter plays a role. By this modification, the adhesion probability differences between a flotation column and a stirred reactor are removed, and the differences in equilibrium adhesion are only due to differences in shear forces prevailing in both systems.

3. Experimental

3.1. Flotation

Flotation experiments are carried out in a modified glass Hallimond tube (Fig. 2), with a length of 30 cm and a diameter of 2.5 cm. In our flotation, column particles and bubbles are transported through tubes to the column. For the experiments, 2 g of a sample is dispersed in 40 ml of liquid. The column is filled with the same liquid. Both the column and the sample slurry are saturated with nitrogen gas or hydrogen gas for 10 min. The slurry ($5\,\mu l\,s^{-1}$) and the bubbles of 1 mm diameter (admitted at a rate of about 20 bubbles per minute) are jointly pumped into the column. The adhering particles are collected at the top of the column and subsequently dispersed in 250 ml water.

The amount of carbon floated is investigated using a Met One particle counter (PCX remote particle counting sensor), using the light blockage principle. Because of the strong light absorption of carbon, it was impossible to use the particle count directly as input for the bubble coverage calculation. A linear correlation was observed between the carbon concentration and the number of carbon particles with a size exceeding 12 μm per unit volume of the dispersion. The particle counter is also used to investigate the particle size distribution before and after the flotation.

From the carbon concentration, the amount of particles per bubble is calculated. When a monolayer coverage is assumed, the bubble coverage can be calculated from the number of adhering particles. Because of the non-spherical nature of the particles and the dense packing of the particles, a void fraction ε of 0.48 is used in calculations.

To investigate the effect of surface tension on the adhesion behaviour various mixtures of ethanol in water (0–17.5%, v/v) are used. The surface tension of the mixtures was measured by using the capillary rise method.

3.2. Materials and preparation

A steam-activated peat based carbon, SX1G, supplied by Norit NV (Amersfoort, The Netherlands) is used for the experiments. The mean particle diameter is assessed using a Coulter counter and equals 20 μm. The density of carbon is obtained from picnometer measurements using water and is equal to $824\,kg\,m^{-3}$.

4. Results and discussion

4.1. Bubble pick up

Particle-to-bubble adhesion experiments under stagnant conditions are performed using the bubble pick up (BPU) experiments. The procedure is described by Vinke et al. [2]. We have used different gases (N_2, H_2, Ar, and He) to investigate the effect of the gas phase on particle to bubble adhesion. Vinke used Pd/C catalyst (Fluka) rather than carbon itself. From bubble pick up experiments, a bubble coverage angle α is obtained, under the assumption of monolayer coverage. Using α the bubble coverage ζ can be calculated as

$$\zeta = 0.5(1-\cos\alpha) \tag{4}$$

The results of our experiments and those of Vinke et al. [2], given in Table 1, show the difference between adhesion in the presence of reactive gases, like H_2 and air, and inert gases like N_2, Ar and He. The use of hydrogen results in a higher bubble coverage than that obtained for inert gases, whereas the use of air results in a lower bubble coverage.

Bubble pick up experiments are also performed using a variety of water–ethanol solutions to establish the impact of surface tension. The results of these

Table 1
The results of BPU experiments using various gases in water

Gas	α (°) for SX1G	α (°) for 10 wt.% Pd/C [2]
H_2	180	180
N_2	117±8	
He	117±7	
Ar	116±7	
Air		102±8

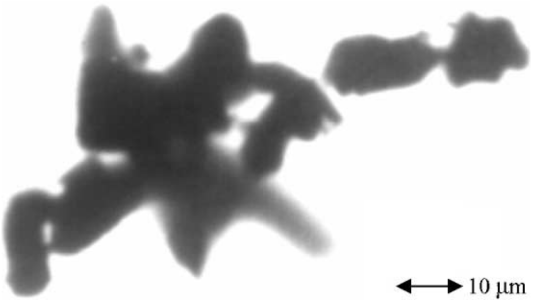

Fig. 4. Light-microscope picture of an SX1G agglomerate. SX1G particles in water.

experiments are given in Fig. 3, illustrating that the difference between hydrogen and nitrogen bubbles is only observed at high surface tensions, and so in pure water.

Van der Zon et al. [1] demonstrated that hydrophobic carbon particles tend to agglomerate in water (see Fig. 4). This agglomeration is also observed under the stagnant conditions in the bubble-pick-up equipment. For liquids with high gas–liquid surface tensions (water) a stronger agglomeration tendency is observed than for liquids having a low surface tension, as ethanol–water mixtures. For low surface tension liquids, the absence of agglomeration results in an equal bubble coverage for nitrogen and hydrogen.

The tendency to form agglomerates is also affected by the presence of hydrogen gas. Under stagnant (BPU) conditions and in water, the particles adhering to nitrogen bubbles show a high degree of agglomeration resulting in beard formation (Fig. 5a). For low surface tension liquids and nitrogen bubbles, as well as for a combination of all liquids investigated and hydrogen bubbles, the agglomeration tendency is less (Fig. 5b). The influence of the gas phase probably arises from adsorption of the gas phase on the carbon surface, affecting the particle–particle interaction as also reported by Rietema [7].

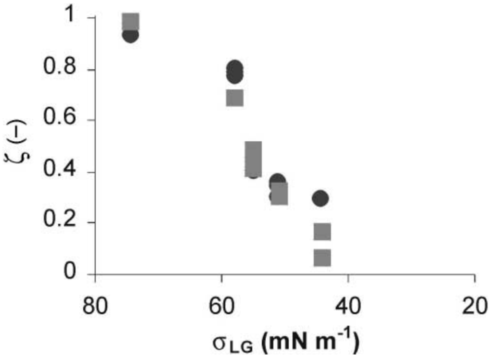

Fig. 6. Bubble coverage as a function of surface tension. Results of flotation of SX1G with N_2 (●) and H_2 (■).

The adhesion of particles is a function of gravity force F_g, buoyancy force F_{bouy}, capillary force F_a and capillary pressure F_s [8]. The force balance may be formulated as

$$0 = -|F_g| + |F_{bouy}| + |F_a| - |F_\sigma| \quad (5)$$

During BPU experiments with nitrogen bubbles and high G–L surface tension, the gravity force is higher

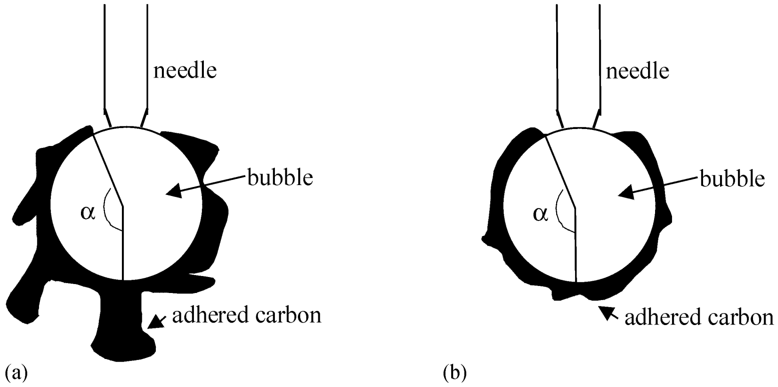

Fig. 5. (a) Schematic representation of a N_2 bubble covered by carbon particles in the BPU in water. (b) Schematic representation of a H_2 bubble covered by carbon particles in the BPU.

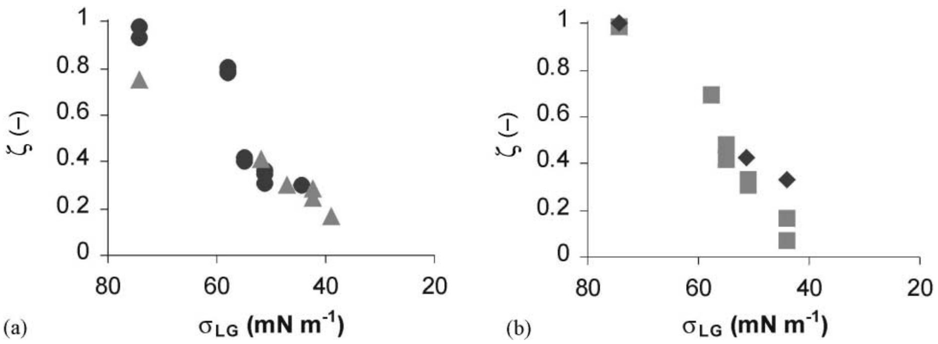

Fig. 7. (a) Bubble coverage as a function of surface tension. A comparison of SX1G BPU (▲) and flotation (●) with N_2. (b) Bubble coverage as a function of surface tension. A comparison of SX1G BPU (◆) and flotation (■) with H_2.

than for hydrogen bubbles, as a result of particle agglomeration, whereas agglomeration tends to reduce the bubble coverage angle α, it may lead to an increased total particle loading. At lower surface tension, less agglomeration occurs, resulting in more similar adhesion behaviour to nitrogen and hydrogen bubbles, respectively.

4.2. Flotation

Flotation results using nitrogen and hydrogen gas for liquids with a varying gas–liquid surface tension are given in Fig. 6. Clearly, under non-stagnant conditions no difference is observed between the bubble coverage of nitrogen and hydrogen bubbles. This is related to the fact that under non-stagnant conditions, multi-layer adhesion (beard formation) is absent or at least greatly reduced.

Fig. 7a and b shows a comparison between the results obtained by BPU and flotation experiments. When comparing the results of flotation to those of the BPU, a small but just significant difference is seen between high surface tension (in water) for nitrogen results (Fig. 7a).

It is important to ascertain whether the modified Hallimond flotation column is representative for

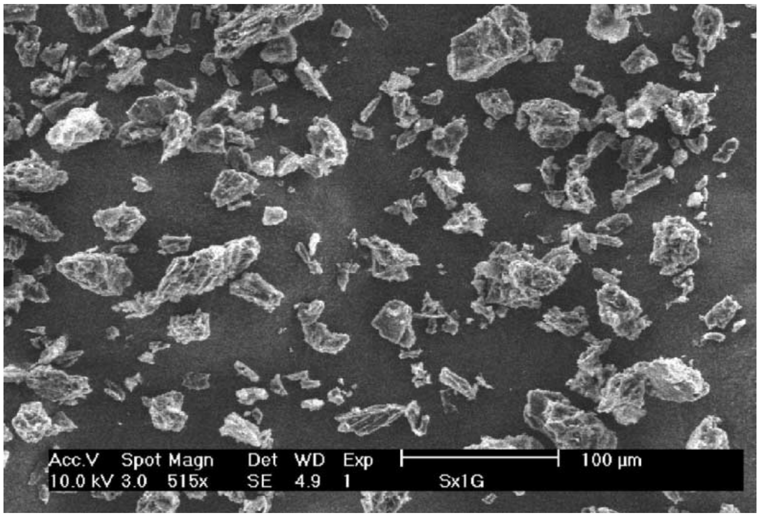

Fig. 8. SEM picture of the SX1G particle size distribution.

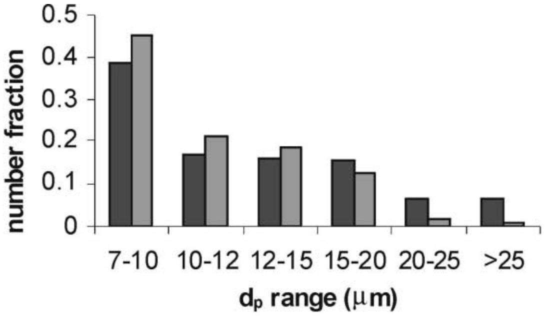

Fig. 9. Number fraction as function of particle diameter for SX1G in water measured with a Met One particle counter. (■): before flotation and (▨): after flotation.

experiments under turbulent conditions in a stirred tank reactor in spite of the fact that the flotation column operates under laminar conditions. As shown in Fig. 1, the flotation probability under turbulent conditions increases, whereas under laminar conditions the flotation probability decreases for smaller particles. This is to be attributed to be caused by differences in collision probability. Because of the flotation probability increases for smaller particles, the particle size distribution after flotation has shifted to lower particle sizes as compared to original particle size distribution.

Fig. 8 shows an SEM picture of SX1G particles prior to flotation, while Fig. 9 shows the measured particle size distributions before and after flotation, illustrating the shift in particle size distribution that occurs during flotation. This shift suggests that the coverage ζ of the bubbles in the modified Hallimond tube is not a function of the collision probability, but only of the adhesion probability. In this case, the flotation column becomes representative for the adhesion behaviour in a stirred turbulent reactor, except for differences in shear forces.

Flotation and bubble pick up experiments were used to analyse the results obtained during the hydrogenation of methyl acrylate using a hydrophobic Pd-on-carbon catalyst in a stirred autoclave. In particular, we wanted to establish whether under turbulent conditions, the G–L mass transfer may also be affected by adhesion of particles to gas bubbles. To this end, the operating conditions were chosen in such a way as to establish full G–L mass transport control. Details of this experimental work and the equations for the film theory based on G–L mass transfer model are presented elsewhere [1]. From this model and a bubble coverage, ζ of 20% at a surface tension of $45\,\mathrm{mN\,m^{-1}}$ may be derived on the basis of experimental mass transfer data. Despite the fact that shear forces in a stirred tank are stronger than in the flotation tube presently used, the bubble coverage found in this way is remarkably close to that obtained by using the flotation column and the BPU equipment as can be seen in Figs. 6 and 7. One may therefore speculate that shear forces may not affect the bubble coverage for particles as small as those presently used.

5. Conclusions

The colloidal properties of solid (catalyst) particles in three phase reactors may have a marked impact on the overall hydrodynamics and G–L mass transfer rates. In the present work, we have investigated the adhesion of carbon catalyst support materials to gas bubbles in an aqueous environment. It is well known that such adhesion may result in enhanced bubble coalescence and increased G–L mass transfer rates. The adhesion behaviour of carbon was studied under stagnant conditions — with single bubbles attached to a capillary (BPU method) — under laminar flow conditions using a modified flotation column, and under reactive conditions in a stirred autoclave, using the mass transfer limited hydrogenation of methyl acrylate, catalysed by Pd-on-carbon.

Adhesion is not only strongly affected by the G–L surface tension and particle size, but also by the composition of the gas phase. Carbon shows a decreasing adhesion tendency in the order $H_2 > N_2 >$ Air. It is shown that the flotation behaviour provides a good qualitative insight into the adhesion in a stirred reactor, and thus for the impact of particle adhesion on the overall mass transfer in a stirred reactor. It was further demonstrated that particle agglomeration significantly affects adhesion, in particular under stagnant conditions and at high G–L surface tensions. Remarkably, agglomeration is also influenced by the composition of the gas phase. It is demonstrated that this is related to the particle–particle interaction. Clearly the phenomenon of particle agglomeration is relevant to catalyst filterability.

Acknowledgements

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