Electronic Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

Selective catalytic oxidation of glycerol – perspectives for high value chemicals.

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We have gathered in Table S1 a collection of criteria used for the evaluation of the importance of the concentration gradient through the external films formed at the interphases ($\alpha_{L/S}$ and $\alpha_{G/L}$ stands respectively for the liquid-solid and gas-liquid interphases) and inside the porous catalyst [φ' as the Weisz modulus (Froment and Bischoff)]. They have been estimated from the results of a selection of studies carried out in similar operating conditions. Note that, contrary to the original papers, we have chosen the Weisz criteria instead of the Thiele modulus because the first one is based on the apparent rate. All the estimations assumed dissolved oxygen as the limiting reactant. Some parameters have been recalculated. Grandientless concentration is reached when all these criteria are below 0.1 (0.3 for the Weisz modulus), indicating that the chemical regime is obtained.

Obviously, the major difficulty lies in the proper estimation of the mass transfer coefficient for the solid external resistances because existing correlations are mainly dedicated to the traditional geometries of reactors. Concerning the gas-liquid mass transfer coefficient, it can be experimentally obtained by physical (absorption-desorption method, residence time distribution analysis, measurement of *in situ* oxygen concentration with dedicated probe) or chemical methods knowing the intrinsic rate.

It is clear from the results that both intraparticular resistance, liquid-solid and gas-liquid resistances can be significant in the reported studies. The chemical regime is therefore not always reached.

Table S1 Criteria used to evaluate the inter- and intra-particle mass transfer resistances applied for the liquid-phase glycerol oxidation from different studies assuming oxygen as the limiting reactant (some parameters have been adapted for this review).

	Demirel *et al.*	Zope *et al.*	Zope *et al.*
Reactor	Slurry batch reactor	Trickle-bed reactor	Slurry batch reactor
Catalyst	Au/C	Au/TiO_2 (WGC)	Au/TiO_2 (WGC)
Temperature	60 °C	60 °C	60 °C
Pressure	10 bars	10 bars	10 bars
NaOH/Gly (mol/mol)	4/1	1/1	1/1
Au/Gly (mol/mol)	1/2500	nd	1/8000
Initial glycerol concentration	150 $mol\cdot m^{-3}$	30 $mol\cdot m^{-3}$	30 $mol\cdot m^{-3}$
Oxygen concentration $C_{O2}^{L,eq}$	10 $mol\cdot m^{-3}$	10 $mol\cdot m^{-3}$	10 $mol\cdot m^{-3}$
Catalyst particles diameter d_P	0.05 mm 1 mm	0.18 mm	0.038 mm
Apparent oxygen rate (liquid volume based)	$r_{O2,p}$ = 0.4 $mol\cdot m_{liq}^{-3}\cdot s^{-1}$	$r_{O2,p}$ = 10.6 $mol\cdot m_{liq}^{-3}\cdot s^{-1}$	$r_{O2,p}$ = 0.02 $mol\cdot m_{liq}^{-3}\cdot s^{-1}$
Apparent oxygen rate (catalyst volume-based)	$r_{O2,p}$ = 39 $mol\cdot m^{-3}{}_{cat}\cdot s^{-1}$	$r_{O2,p}$ = 15 $mol\cdot m^{-3}{}_{cat}\cdot s^{-1}$	$r_{O2,p}$ = 80 $mol\cdot m^{-3}{}_{cat}\cdot s^{-1}$
Effective oxygen diffusivity in the catalyst	$D_{e,O2} = 6.8\cdot10^{-10}\ m^2\cdot s^{-1}$	$D_{e,O2} = 4\cdot10^{-10}\ m^2\cdot s^{-1}$	$D_{e,O2} = 4\cdot10^{-10}\ m^2\cdot s^{-1}$
Gas-liquid mass transfer coefficient	$k_La = 0.465\ s^{-1}$	$k_La = 0.61\ s^{-1}$	
Liquid-solid mass transfer coefficient	$k_{L/S} = 7.7\cdot10^{-2}\ m.s^{-1}$ ($d_P = 50\cdot10^{-3}$ mm) $k_{L/S} = 0.4\cdot10^{-2}\ m.s^{-1}$ (d_P = 1 mm)	$k_{L/S} = 1.1\cdot10^{-4}\ m\cdot s^{-1}$	
Intraparticle resistance $\varphi' = \frac{\bar{r}_{O_2,P} L_p^2}{D_{e,O_2} C_{O_2}^{eq,L}}$ φ' < 0.3	0.002 ($d_P = 50.10^{-3}$ mm) 0.04 (d_P = 1 mm)	3.6	0.8
Liquid-solid resistance $\alpha_{L/S} = \frac{\bar{r}_{O_2,p} L_p}{k_{L/S,O_2} C_{O_2}^{L,eq}}$ $\alpha_{L/S} < 0.1$	10^{-6} ($d_P = 50\cdot10^{-3}$ mm) $6\cdot10^{-4}$ (d_P = 1 mm)	0.43	nd
Gas-liquid resistance $\alpha_{G/L} = \frac{\bar{r}_{O_2,p}}{k_L a \times C_{O_2}^{L,eq}}$ $\alpha_{G/L} < 0.1$	0.085	0.14	nd