Enhancing the Capacity of Oxygen Carriers for Selective Oxidations through Phase Cooperation: Bismuth Oxide and Ceria-Zirconia

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Supporting Information

S1 Influence of Heat and Mass Transfer on the Measured Kinetics

This section describes a set of standard diagnostic criteria used to determine whether a particular transport phenomenon could have influenced the measured kinetics (*viz.* cause a deviation from the intrinsic kinetics by more than 5 %).[1]

S1.1 Axial Dispersion

The flux of chemical species due to axial dispersion in a packed bed can act to decrease the apparent rate of reaction. The following criterion is satisfied if the effect of axial dispersion can be neglected[2,3]:

$$\frac{h_{bed}}{d_p} > \frac{8}{Bo} n \ln \frac{1}{1 - X} \tag{S1}$$

where h_{bed} is the axial length of the reactive bed (including inert diluting particles), d_p is the particle diameter, $Bo \equiv ud_p/D_{ax}$ is the Bodenstein number, u is the superficial velocity of the gas, D_{ax} is the axial dispersion coefficient, $n = 1$ is the order of reaction, and X is the conversion of the reactant. D_{ax} was calculated using a correlation reported by Delgado (2006, equations 18 and 19).[4]

S1.2 Bed Dilution

Bed dilution is the mixing of reactive particles with inert particles, and is used to alleviate the effects of heat transfer across the bed. However, bed dilution itself can influence the rate of reaction due to local bypass effects. The following criterion is satisfied if the effect of bed dilution can be neglected[5]:

$$b < \frac{1}{1 + 10Xd_p/h_{bed}} \tag{S2}$$

where b is the volume of inert particles as a fraction of the total volume of solids.

S1.3 External Mass Transfer

Diffusion through the stagnant film surrounding the reactive particles (*i.e.* external mass transfer) can limit the observed rate of reaction. The following criterion is satisfied if the effect of external mass transfer can be neglected[6]:

$$\frac{r_{v,obs}}{k_g a C_{bulk}} < \frac{0.05}{n} \tag{S3}$$

where $r_{v,obs}$ is the observed rate of reaction per unit volume of reactive particle, k_g is the external mass transfer coefficient, a is the external surface area per unit volume of reactive particle, C_{bulk} is the concentration of the reactant in the bulk, and $C_{surface}$ is the concentration of the reactant at the external surface of the particle. k_g was calculated using a correlation reported by Wakao and Funazkri (1978).[7]

S1.4 Internal Mass Transfer

Diffusion within the pores of the reactive particles (*i.e.* internal mass transfer) can limit the observed rate of reaction. The following criterion is satisfied if the effect of internal mass transfer can be neglected for a first order reaction[8]:

$$\frac{r_{v,obs}\left(d_p/6\right)^2}{C_{surface}D_{eff}} < 0.067 \tag{S4}$$

where D_{eff} is the effective diffusivity of the reactant within the pores of the particle, and was calculated using:

$$D_{eff} = \frac{\varepsilon_p}{\tau} D_m \tag{S5}$$

where ε_p is the porosity of the particle, τ is the tortuosity of the pores and D_m is the molecular diffusivity of the reactant. D_m was calculated according to Chapman-Enskog theory.[9] The absence of limitations due to external mass transfer means $C_{surface} = C_{bulk}$.

S1.5 Radial Heat Transfer across the Bed

Interparticle heat transfer along the radius of the bed may be neglected if the following criterion is satisfied[10]:

$$\frac{r_{v,obs}\left|\Delta_r H\right|(1-\varepsilon_b)(1-b)d_t^2}{32\lambda_{eff,r}} < \frac{0.05RT^2}{E_a} \tag{S6}$$

where $\Delta_r H$ is the enthalpy of reaction, ε_b is the voidage of the bed, d_t is the diameter of the bed, $\lambda_{eff,r}$ is the effective radial thermal conductivity of the bed, R is the molar gas constant, T is the temperature of the bed and E_a is the apparent activation energy of the reaction. $\lambda_{eff,r}$ was calculated using a correlation reported by Specchia *et al.* (1980).[11]

S1.6 External Heat Transfer

Conduction of heat through the stagnant film surrounding the reactive particles (i.e. external heat transfer) can affect the observed rate of reaction. The following criterion is satisfied if the effect of external heat transfer can be neglected[10]:

$$\frac{r_{v,obs}|\Delta_r H| d_p^2}{6\alpha_p} < \frac{0.05RT^2}{E_a} \tag{S7}$$

where α_p is the heat transfer coefficient between the particle and the bulk gas. α_p was calculated using a correlation by Wakao and Funazkri (1979).[12]

S1.7 Internal Heat Transfer

Conduction of heat through the pores of the reactive particles (*i.e.* internal heat transfer) can affect the observed rate of reaction. The following criterion is satisfied if the effect of internal heat transfer can be neglected[10]:

$$\frac{r_{v,obs}|\Delta_r H| d_p^2}{60\lambda_p} < \frac{0.05RT^2}{E_a} \tag{S8}$$

where λ_p is the thermal conductivity of the reactive particle. λ_p was estimated conservatively to be 0.1 W m^{-1} K^{-1}.[13]

S1.8 Evaluation of Criteria

Table S1 shows the variables and parameters evaluated for the experiment conducted for Bi25Ce100Zr at 475°C (corresponding to the highest measured k_{H_2}, which is most susceptible to transport limitations). Table S2 shows the evaluation of the criteria applied to this experiment, and it can be seen that all criteria were satisfied and that the measured rates of reaction reflected the intrinsic kinetics.

Table S1: Variables used in the evaluation of the diagnostic criteria. Experimental conditions: total flow of 465 mL/min (as measured at 293 K, 1 atm) of 4.81 vol% H_2 in balance N_2, bed contains 0.0129 g of Bi25Ce100Zr of size 90 – 150 μm, temperature 748 K, pressure 1 atm.

Variable	Value		Ref.	Comments
a	5.16×10^{4}	$m^2\ m^{-3}$		Assumed spherical particles
b	0.95			
C_{bulk}	0.773	$mol\ m^{-3}$		
C_p	1.1	$kJ\ kg^{-1}\ K^{-1}$		Isobaric heat capacity of N_2
$C_{surface}$	0.773	$mol\ m^{-3}$		Valid because criterion S3 applied
D_{ax}	2.2×10^{-4}	$m^2\ s^{-1}$	[4]	Comparable to D_m, but criterion S1 was insensitive to deviations in D_{ax} of at least 500%
D_{eff}	1.0×10^{-4}	$m^2\ s^{-1}$		
D_m	3.6×10^{-4}	$m^2\ s^{-1}$	[9]	
d_p	116	μm		
d_t	8	mm		
E_a	100	$kJ\ mol^{-1}$		Conservative estimate. Measured value was 80 $kJ\ mol^{-1}$
h_{bed}	4	mm		
k_g	7.6	$m\ s^{-1}$	[7]	
n	1			
u	0.39	$m\ s^{-1}$		
$r_{v,obs}$	178	$mol\ m^{-3}\ s^{-1}$		
T	748	K		
X	0.0724			
α_p	1100	$W\ m^{-2}\ K^{-1}$	[12]	
$\Delta_r H$	-51	$kJ\ mol^{-1}$	[14]	Reaction: $\frac{1}{3}Bi_2O_{3(s)} + H_{2(g)} \rightleftharpoons \frac{2}{3}Bi_{(l)} + H_2O_{(g)}$
ε_b	0.38			Estimated, typical value
ε_p	0.4			Conservative estimate. Criterion S4 was insensitive for $\varepsilon_p > 0.006$
$\lambda_{eff,r}$	0.6	$W\ m^{-1}\ K^{-1}$	[11]	
λ_g	0.049	$W\ m^{-1}\ K^{-1}$	[9]	Thermal conductivity of gas, from Eucken formula
λ_{inert}	97	$W\ m^{-1}\ K^{-1}$	[15]	Thermal conductivity of SiC particles
λ_p	0.1	$W\ m^{-1}\ K^{-1}$	[13]	Conservative estimate
μ	3.3×10^{-5}	Pa s	[9]	Dynamic viscosity of gas, from Chapman-Enskog theory
ρ	0.436	$kg\ m^{-3}$		Density of gas
τ	1.4			Estimated, typical value

Table S2: Evaluation of the diagnostic criteria using the values reported in Table S1, establishing the absence of significant deviations from the intrinsic kinetics.

Criterion		LHS	RHS
$\frac{h_{bed}}{d_p} > \frac{8}{Bo} n \ln \frac{1}{1-X}$	(S1)	34	2.9
$b < \frac{1}{1+10Xd_p/h_{bed}}$	(S2)	0.95	0.98
$\frac{r_{v,obs}}{k_g a C_{bulk}} < \frac{0.05}{n}$	(S3)	5.8×10^{-4}	0.05
$\frac{r_{v,obs}(d_p/6)^2}{C_{surface}D_{eff}} < 0.067$	(S4)	8.6×10^{-4}	0.067
$\frac{r_{v,obs}\lvert\Delta_r H\rvert(1-\varepsilon_b)(1-b)d_t^2}{32\lambda_{eff,r}} < \frac{0.05RT^2}{E_a}$	(S6)	0.9 K	2.3 K
$\frac{r_{v,obs}\lvert\Delta_r H\rvert d_p^2}{6\alpha_p} < \frac{0.05RT^2}{E_a}$	(S7)	0.2 K	2.3 K
$\frac{r_{v,obs}\lvert\Delta_r H\rvert d_p^2}{60\lambda_p} < \frac{0.05RT^2}{E_a}$	(S8)	0.02 K	2.3 K

S2 Limitation of the sensor response time on the measured kinetics

In general, measurements of the rates of gas-solid reactions could be influenced by limitations in heat and mass transfer and also by the response of the analysers. Estimates of the rates of heat and mass transfer, and qualification with standard diagnostic criteria, indicate that the rates of reaction were not likely to have been influenced by these phenomena. To estimate the impact on the rate of reaction due to convolution with the response of the sensor, a characteristic reaction time, τ, was defined:

$$\tau = t(y = \max(y)e^{-1}) - t_{start} \qquad \text{(S9)}$$

i.e. τ is the time taken for the rate of reaction to fall to a factor of $e^{-1} = 0.368$ from the maximum, measured from the start of the reaction. The ratio of the reaction time to the response time, τ/t_{mix}, then gives an indication of how severely the measurements were affected by convolution with the sensor; these are summarised in Table S3 for the kinetic measurements. It can be seen that the humidity sensor responds sufficiently quickly for samples Bi25Ce0Zr, Bi25Ce25Zr and Bi25Ce50Zr, because τ/t_{mix} is an order of magnitude greater than unity. The samples richer in ceria (Bi25Ce75Zr and Bi25Ce100Zr) reacted much quicker, such that τ/t_{mix} was closer to unity. For these samples, the response time may have affected the kinetic measurements despite the deconvolution procedure, but probably not to a significant extent.

Table S3: Characteristic reaction times compared to the response time of the humidity sensor, appropriate for the kinetic experiments.

	450°C		500°C		550°C	
	τ	τ/t_{mix}	τ	τ/t_{mix}	τ	τ/t_{mix}
	s	-	s	-	s	-
Bi25Ce0Zr	124	11	69	15	37	10
Bi25Ce25Zr	179	16	70	14	38	11
Bi25Ce50Zr	122	11	54	9	26	7
Bi25Ce75Zr	59	5	22	6	-	
Bi25Ce100Zr	24	4	16[a]	5[a]	-	

[a] Measurement was taken at 475°C

S3 X-ray Photoelectron Spectroscopy (XPS)

The oxygen-free mole fraction of species *i*, x_i, was calculated using:

$$x_i = \frac{n_i}{\sum_{i \neq oxygen} n_i} = \frac{n_i}{n_{Ce} + n_{Zr} + n_{Bi}} \qquad (S9)$$

where n_i is the mole fraction of species i measured by XPS. n_i was calculated from the spectra by fitting characteristic peaks from each element and their relative sensitivity factors. The peaks used were Ce 3d, Zr 3d and Bi 4f.

S4 References

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