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CORRECTION

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Correction: Surface reaction kinetics of the methanol synthesis and the water gas shift reaction on $Cu/ZnO/Al_2O_3$

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Correction for 'Surface reaction kinetics of the methanol synthesis and the water gas shift reaction on $Cu/ZnO/Al_2O_3$' by Bruno Lacerda de Oliveira Campos *et al.*, *React. Chem. Eng.*, 2021, **6**, 868–887; DOI: 10.1039/D1RE00040C

A mistake was found in the Matlab program used for the simulations. That is, a parameter of the Gibbs free energy change of zinc reduction ($\Delta G^0_{Zn\ red.}$) was wrongly typed, which participates in eqn (31) and (37) of the original paper. $\Delta G^0_{Zn\ red.}$ is calculated from the thermodynamic data of Goos *et al.*,[1] and the equation with the correct data is as follows.

$$\Delta G^0_{Zn\ red.} = R\cdot[8411.4 - 8.3237\cdot T + 1.9335\times10^{-4}\cdot T^2 - 2.2728\times10^{-7}\cdot T^3 - 4.3047\times10^{-10}\cdot T^4 + 1.6777\times10^{-13}\cdot T^5 + 0.9824\cdot T\cdot\ln(T)] \quad (1)$$

With the corrected parameter, the zinc solubility in copper (X_{Zn}) and, consequently, the zinc coverage (ϕ_{Zn}) have lower values than the originally published ones, as shown in the revised Fig. 4.

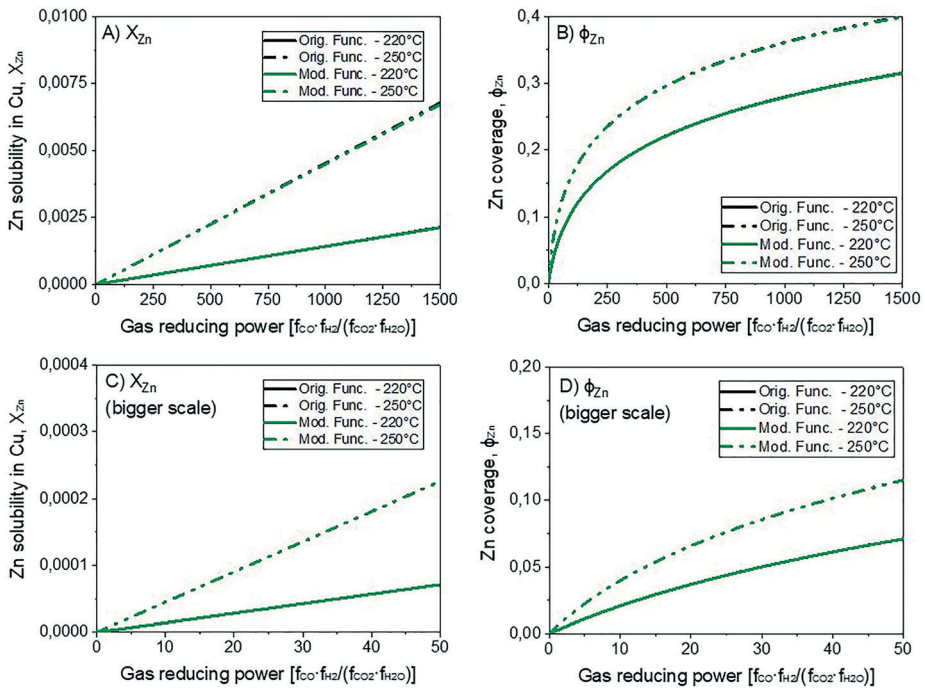

Fig. 4 Solubility of zinc in the Cu-bulk (A and C) and zinc coverage (B and D) as functions of the gas reducing power.

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With the corrected parameter, new simulations of the experiments were performed, with the normalized residues and statistical indicators shown in the revised Fig. 6 and Table 4, respectively. The deviations after the parameter correction (χ^2 = 120.67) are in fact higher than that originally published (χ^2 = 74.74).

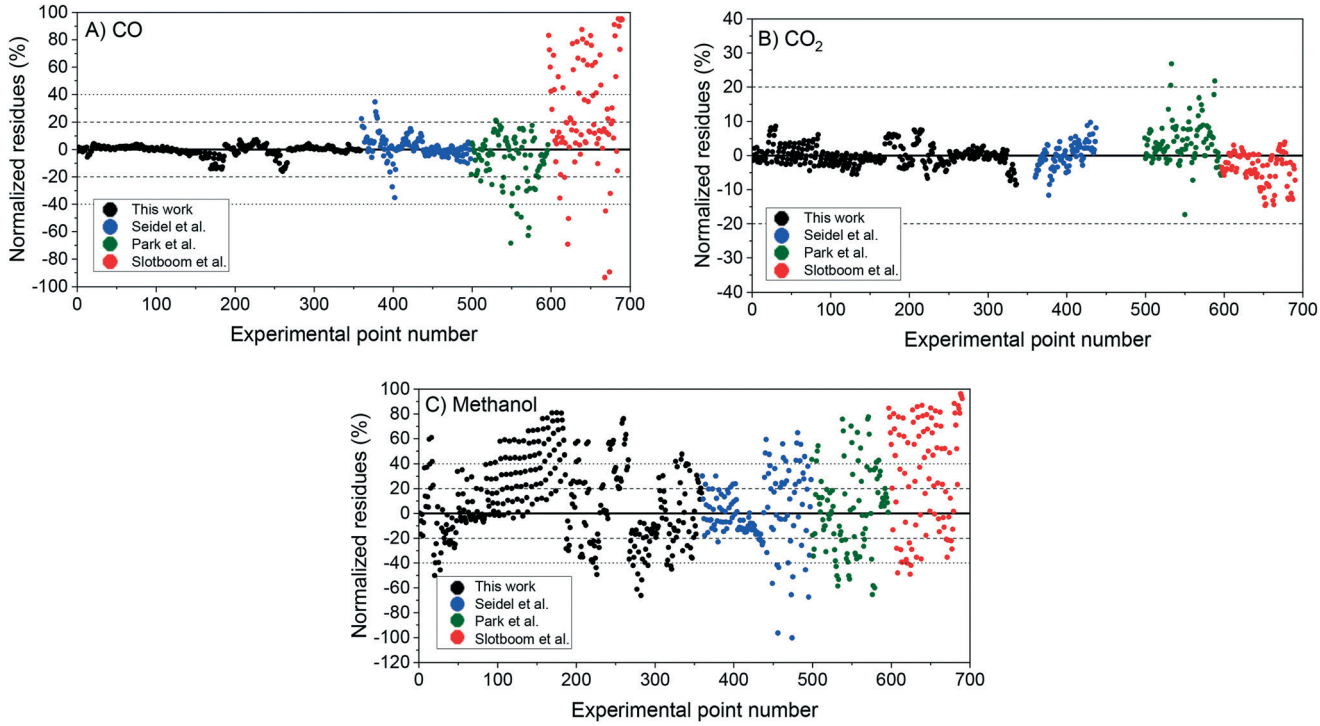

Fig. 6 Two-case model simulation: normalized residues of the simulation of the experiments from this work (1–359), from Seidel *et al.*[2] (360–498), from Park *et al.*[3] (499–596), and from Slotboom *et al.*[4] (597–690). A) Carbon monoxide. B) Carbon dioxide. C) Methanol.

Table 4 Statistical indicators of the model performance in predicting the carbon-containing compounds

Feed:		$H_2/CO/CO_2$			H_2/CO		H_2/CO_2		
Data:		This work	Seidel *et al.*	Park *et al.*	This work	Seidel *et al.*	Seidel *et al.*	Slotboom *et al.*	All
N° of points		324	46	98	35	61	32	94	690
χ^2		38.63	1.45	17.62	2.44	9.29	1.26	49.98	120.67
CO	ME	0.0275	0.0698	0.1481	0.0105	0.0269	0.1010	0.3752	0.0973
	MSE	0.0017	0.0097	0.0526	0.0002	0.0013	0.0164	0.2324	0.0415
CO_2	ME	0.0215	0.0292	0.0537			0.0315	0.0441	0.0315
	MSE	0.0008	0.0013	0.0056			0.0016	0.0036	0.0021
CH_3OH	ME	0.2732	0.1283	0.2831	0.2300	0.3220	0.1198	0.4672	0.2864
	MSE	0.1167	0.0204	0.1216	0.0698	0.1510	0.0190	0.2957	0.1315

By using a constant zinc coverage approach, the model accuracy is improved and the complexity of the model decreases. As it is known that the zinc coverage on the catalyst is reduced by an increase in the CO_2/CO_X ratio $\left(\bar{y}^0_{CO_2}\right)$,[5,6] we divide the operating region into three sectors, the 1st with very low CO_2 content $\left(\bar{y}^0_{CO_2} < 0.001\right)$, the 2nd with very high CO_2 content $\left(\bar{y}^0_{CO_2} > 0.90\right)$, and the 3rd being an intermediate region $\left(0.001 \le \bar{y}^0_{CO_2} \le 0.90\right)$. For each sector, a separate constant zinc coverage was determined, as shown in Table 5.

Table 5 Zinc coverage value depending on the CO_2 to CO_X ratio in the feed

Condition	Zn value
CO_2/CO_X ratio < 0.001	0.90 (for Campos' data) 0.95 (for Seidel's data)
$0.001 \leq CO_2/CO_X$ ratio ≤ 0.90	0.50
CO_2/CO_X ratio > 0.90	0.10

With this approach, corresponding simulations were repeated, and results are shown regarding the normalized residues (Fig. 16), methanol output concentration for selected experiments (Fig. 17), and statistical indicators (Table 6). The overall model performance is thereby improved (χ^2 = 75.97 against 120.67 with Kuld's method[7]), in particular for the intermediate region $\left(0.001 \leq \overline{y}^0_{CO_2} \leq 0.90\right)$.

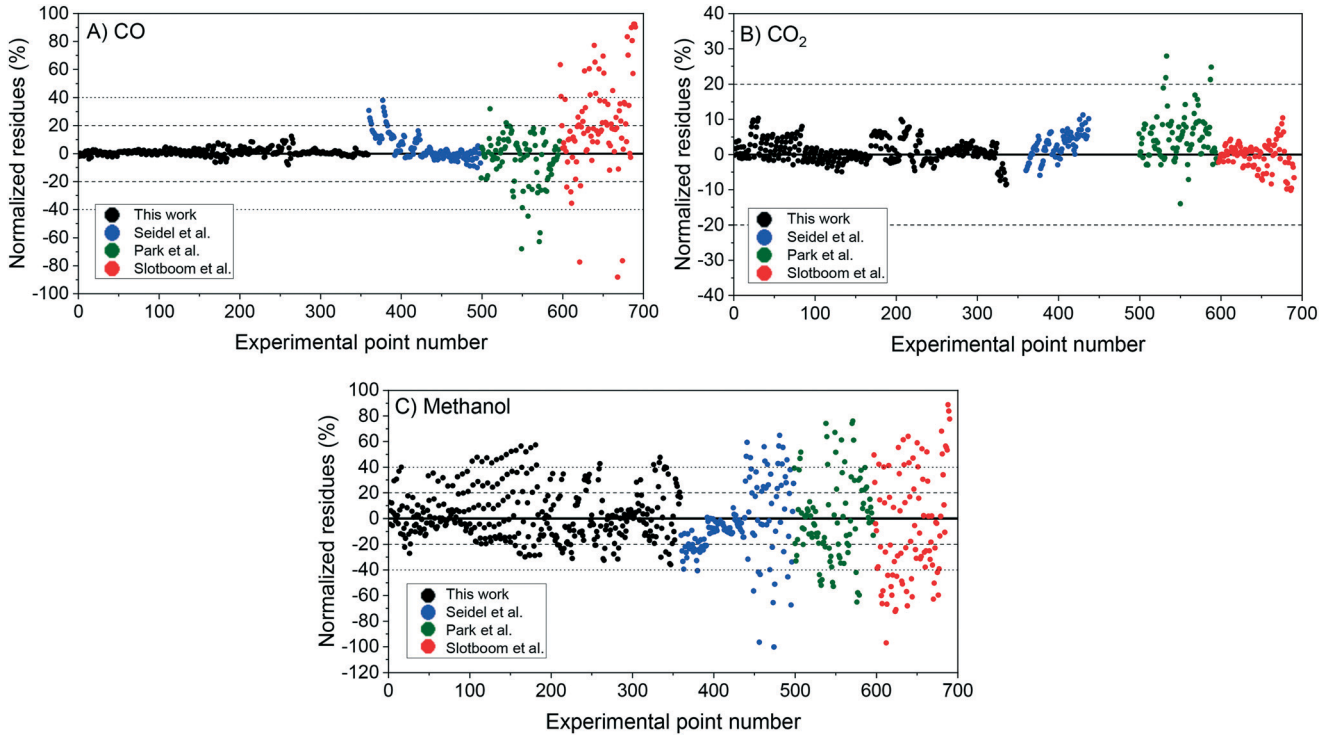

Fig. 16 Two-case model simulation: normalized residues of the simulation of the experiments from this work (1–359), from Seidel *et al.*[2] (360–498), from Park *et al.*[3] (499–596), and from Slotboom *et al.*[4] (597–690). A) Carbon monoxide. B) Carbon dioxide. C) Methanol.

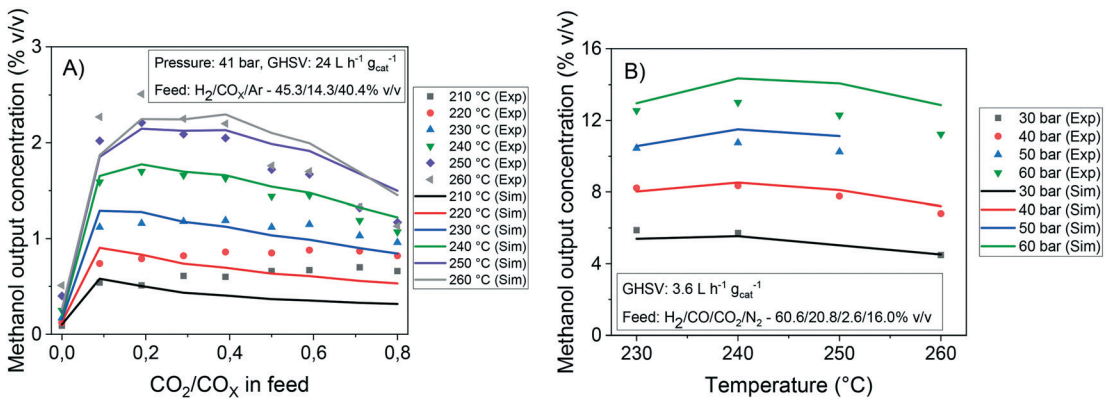

Fig. 17 Experimental and simulated values of the methanol output concentration under different conditions. Databases: A) this work, B) Seidel *et al.*[2]

Table 6 Statistical indicators of the model performance in predicting the carbon-containing compounds

Feed:		$H_2/CO/CO_2$			H_2/CO		H_2/CO_2		
Data:		This work	Seidel *et al.*	Park *et al.*	This work	Seidel *et al.*	Seidel *et al.*	Slotboom *et al.*	All
N° of points		324	46	98	35	61	32	94	690
χ^2		13.05	0.55	15.31	2.44	9.29	3.02	32.31	75.97
CO	ME	0.0192	0.0431	0.1371	0.0105	0.0269	0.1751	0.2978	0.0830
	MSE	0.0008	0.0035	0.0444	0.0002	0.0013	0.0342	0.1530	0.0295
CO_2	ME	0.0227	0.0430	0.0601			0.0301	0.0309	0.0321
	MSE	0.0010	0.0027	0.0067			0.0011	0.0017	0.0022
CH_3OH	ME	0.1499	0.0643	0.2559	0.2299	0.3220	0.2275	0.3749	0.2128
	MSE	0.0385	0.0057	0.1051	0.0695	0.1510	0.0535	0.1890	0.0785

The reaction flow analysis and the sensitivity analysis have no significant changes compared to the originally published ones, with the exception being the zinc coverage profile, which has now constant values. The revised Fig. 11 is given below:

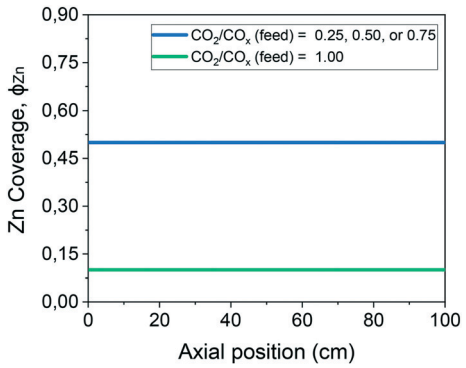

Fig. 11 Zinc coverage along the methanol synthesis reactor with a length of 100 cm. Operating conditions: 220 °C, 60 bar, GHSV = 4.8 $L_S\ h^{-1}\ g_{cat}^{-1}$, feed concentration: H_2/CO_x = 80/20% v/v.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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