

CORRIGENDUM

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**Selective Adsorption of Manganese
onto Rhodium for Optimized Mn/Rh/
SiO₂ Alcohol Synthesis Catalysts**

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The authors would like to correct a mistake made in the calculation of the TOF numbers presented in Table 2. The corrected values provided here include a correction to the original calculation in Table 2 regarding the gas flow rate (resulting in a substantial change in the calculated TOF) and an additional correction based on CO chemisorption experiments (as opposed to using a hemispherical model for the surface area based on the TEM measurements). The results of the chemisorption experiments are reported in Table S1 based on a 1:1 CO/Rh stoichiometry and indicate that the dispersions of the three catalyst samples are quite similar. CO chemisorption measurements were performed at the CleanCat Core facility at Northwestern University by using an Altamira Instruments BenchCAT 1000HP. Catalysts (0.2–0.3 g) were loaded into a U-shaped quartz reactor tube, which was weighed before and after sample addition to ensure an accurate weight measurement. This tube was then loaded into the furnace. Each catalyst was reduced at 300 °C for 2 h (10 °C min⁻¹ ramp rate), then flushed for 30 min in He. 5%CO/He was then pulsed (595 μL loop volume) into the system 15–20 times at 30 °C to ensure the surface was saturated. Each spectrum was integrated to find the volume of CO remaining following adsorption. Surface saturation was typically reached within 10 pulses. The authors would like to thank Neil Schweitzer of the Center for Catalysis and Surface Science, Northwestern University, Illinois and David Childers of the University of Illinois at Chicago for their help with the chemisorption measurements.

Although the chemisorption measurements indicate a lower dispersion for the incipient wetness impregnation (IWI)-prepared sample than may be supposed based on particle size, the Mn promoter likely blocks some sites for CO adsorption if IWI is the technique used for promoter addition. The corrected result does indicate that the samples synthesized by IWI have slightly higher TOFs than those synthesized by using strong electrostatic adsorption (SEA). However, the original paper focuses on the differences in selectivity, therefore, the correction does not influence the conclusions of the original paper.

In addition, the authors wish to correct an error in Figure 7. The edge position of the Rh₂O₃ standard was misaligned and has been fixed, in agreement with existing literature.^[1] A new version of Figure 7 is provided below. The correction does not change the assignment of the state of Rh in the Mn-promoted Rh/SiO₂ catalysts.

We wish to thank the anonymous reviewer (of a more recent paper on RhMn/C nanotubes),^[2] who pointed out our errors.

[1] M. R. Gogate, R. J. Davis, *ChemCatChem* **2009**, *1*, 295–303.

[2] J. J. Liu, Z. Guo, D. Childers, N. Schweitzer, C. L. Marshall, R. F. Klie, J. T. Miller, R. J. Meyer, *Journal of Catalysis* **2014**, *313*, 149–158.

Table 2. Conversion of syngas over promoted and unpromoted Rh catalysts supported on silica.

Catalyst	CO conv. ^[a] [%]	TOF ^[b] [s ⁻¹]	E ^[a,c] [%]	A ^[a,d] [%]	M ^[a,e] [%]	L ^[a,f] [%]	O ^[a,g] [%]
3%Rh/SiO ₂	4.3	0.012	–	–	30	70	–
1%Mn _{SEA}	6.8	0.068	19.1	15.2	41.0	4.8	20.0
3%Rh/SiO ₂	8.3	0.064	18.0	12.5	40.3	5.8	23.6
	11.0	0.070	18.0	10.0	44.1	6.6	21.9
	13.2	0.061	20.4	8.7	37.0	6.4	27.6
	18.2	0.067	17.8	7.1	42.5	6.0	26.6
	24.5	0.068	17.8	5.0	47.3	6.8	23.0
	36.4	0.067	14.6	3.3	52.3	1.8	25.0
	45.0	0.063	14.3	3.9	50.2	1.6	18.1
1%Mn _{IWI}	7.5	0.081	4.8	8.4	17.5	51.2	18.1
3%Rh/SiO ₂	8.8	0.077	5.3	8.4	19.9	49.2	17.3
	10.8	0.079	4.5	7.5	20.6	50.6	16.9
	14.5	0.075	5.8	7.6	23.6	46.5	16.6
	19.0	0.079	6.0	7.6	23.2	46.9	16.4
	27.0	0.085	5.6	3.6	16.7	28.9	33.0
	42.0	0.087	5.0	2.5	20.5	18.8	28.5

[a] The CO conversions were calculated by using nitrogen gas as the internal standard and the equation:

CO Conversion [%] = $(M_{\text{CO feed}} - M_{\text{N}_2 \text{ feed}} / M_{\text{N}_2 \text{ product}} M_{\text{CO product}}) / M_{\text{CO feed}} \cdot 100\%$
in which M_i is the mole percent of component i . The selectivity to product i is based on the total number of carbon atoms among the total products and is defined as:

$$\text{Selectivity}_i [\%] = (n_i M_i) / (\sum n_i M_i) \cdot 100\%$$

in which n_i is the number of carbon atoms, and M_i is the mole percent of product i detected downstream. [b] The TOF is calculated as CO conversion per site per second. The dispersion of Rh particles was determined by using CO chemisorption (1:1 CO/Rh site). [c] Selectivity for ethanol; [d] Selectivity for acetaldehyde; [e] Selectivity for methane; [f] Selectivity for light hydrocarbons C₃₊; [g] Selectivity for acetic acids and C₃₊ oxygenates.

Table S1. Dispersion of catalysts measured by CO chemisorption.

Catalyst	Dispersion [%]
1%Mn _{SEA} 3%Rh/SiO ₂	57.1
1%Mn _{IWI} 3%Rh/SiO ₂	50.8
3%Rh/SiO ₂	50.1

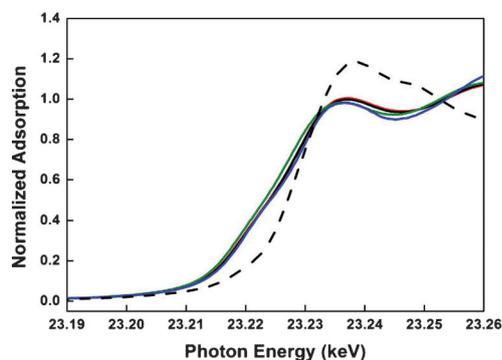


Figure 7. XANES spectrum of Rh K-edge of 1 wt% Mn promoted 3 wt% Rh/SiO₂ catalysts plotted with appropriate standards: Rh₂O₃ reference (-----), 1%Mn_{SEA}3%Rh/SiO₂ catalyst (—), 1%Mn_{IWI}3%Rh/SiO₂ catalyst (—), 3%Rh/SiO₂ catalyst (—), and Rh foil reference (—).