Supplementary Information

Improved NOx Reduction Using C_3H_8 and H_2 with Ag/Al_2O_3 Catalysts Promoted with Pt and WOx

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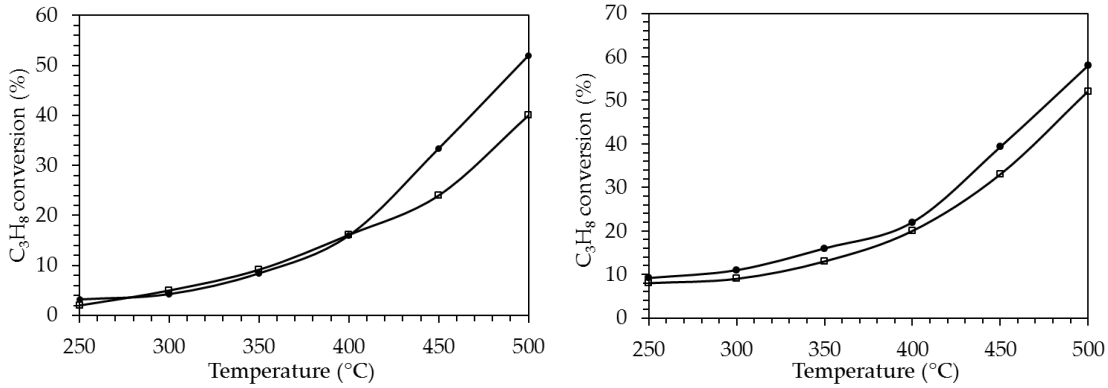
SI.1. WOx promoter effect on Pt in the combustion of C_3H_8

To independently study how W stabilizes the Pt/Al_2O_3 catalyst during the combustion of C_3H_8 in air, the catalysts 0.4Pt/A (without W) and 0.4Pt/AW (with W) were subjected to pre-reduction in H_2 at 500 and 800°C (Pt sintering). The catalysts were evaluated under the following conditions: 300cm³/min of air mixture flow containing 999 ppm of C_3H_8 and 20 mg of catalyst.

The stabilizing effect of the addition of tungsten oxides (WOx) on Al_2O_3 of the 0.4Pt/AW catalyst can be seen in Figure A1 (a-d). Due to the H_2 reduction process up to 800°C (sintering of the Pt), there is a decrease in the dispersion of the Pt that exists when the catalyst has been reduced with H_2 at 800°C and 500°C. Consequently, a decrease in C_3H_8 conversion was observed at temperatures above 400°C (Figure A1 (a)). This decrease was not as noticeable when WOx was added to the 0.4Pt/AW catalyst (Figure A1 (b)).



(**a**) (**b**)

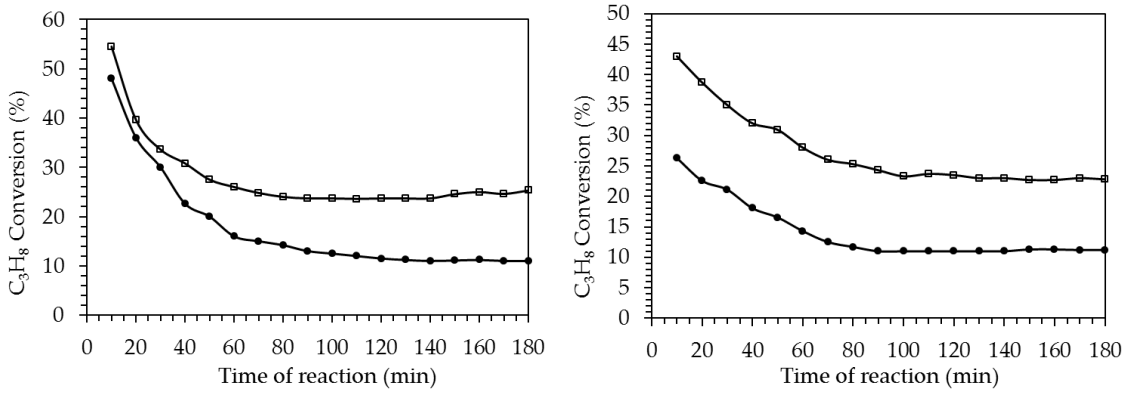


Figure S1. C_3H_8 combustion in air over the (●) 0.4Pt/A; (□) 0.4Pt/AW catalysts reduced to 500 and 800°C. (**a**) Effect of reduction temperature on catalyst 0.4Pt/A without W; (**b**) Effect of reduction temperature on catalyst 0.4Pt/AW with W; (**c**) Effect of WOx during catalyst deactivation 0.4Pt/A without W and 0.4Pt/AW with W reduced to 500°C and (**d**) Effect of WOx during deactivation of 0.4Pt/A catalysts without W and 0.4Pt/AW with W reduced to 800°C. Evaluation conditions: 300cm^3/min of air mixture flow plus 999 ppm of C_3H_8, catalyst weight: 20 mg.

The effect of the WOx promoter during the C_3H_8 combustion deactivation process can also be observed in the two catalysts when they were reduced to 500°C (Figure A1 (c)) and when they were reduced to 800°C (Figure A1 (d)). In both cases, it was observed that the 0.4Pt/AW catalyst promoted with W showed shower higher stability. As has been reported in the literature [43,44], the addition of WOx to Al_2O_3 stabilizes the Pt particles (see Figure A2). With this, the high temperatures (> 500°C) will not strongly affect Pt and Ag dispersion.

SI.2. Weisz-Prater criterion to evaluate internal mass transfer limitations in catalysts.

The C_{WP} criterion establishes that if $C_{WP} < 1$ is fulfilled, there are no diffusion mass transfer limitations, and therefore there is no significant concentration gradient within the granules. Thus it can be ensured that reaction rates are being obtained in a reactor in kinetic regime.

The Weisz-Prater (CWP) criterion uses the measured values of the reaction rate (-ra) to determine whether internal diffusion is limiting the evaluated reaction rate [63]:

$$C_{WP} = \frac{-r_a \, \rho_c \, R^2}{De \; C_{as}} \qquad S1$$

This criterion requires the following variables:

$-r_a$ = Reaction rate (mol/g_c.s)

ϱ_c = Catalyst granule density (g/cm^3)

R = Radius of the particle (cm)

De = Effective diffusivity (cm^2/s)

Using the pore model in disorder [64]

$$De = D_M \varepsilon_M^2 + [\varepsilon_\mu^2(1 + 3\varepsilon_M)/(1- \varepsilon_\mu)]D_\mu \qquad S2$$

D_M = Combined diffusivity in the macropores (cm^2/s)

D_μ = Combined diffusivity in the micropores (cm^2/s)

ε_M = Porosity in the in the macropore region [in our catalysts, ε_M = 0.61 for a catalyst granule density of 0.417 (g_c/cm^3)][64]

ε_μ = Porosity in the in the micropore region = 0

The combined diffusivity in the macropores D_M was calculated as:

$$D_M = 1/[1/D_{NO\text{-}N2} + 1/(D_K)_{NO}] \quad \text{S3}$$

Where $D_{NO\text{-}N2}$ was calculated by the Chapman-Enskog formula [64]:

$$D_{NO\text{-}N2} = (0.0018583)[[\ T^{3/2}(1/M_{NO}+1/M_{N2})^{1/2}\ ]/\ (Pt\ \sigma^2_{NO\text{-}N2}\ \Omega_{NO\text{-}N2})] = \quad \text{S4}$$

and the Knudsen diffusivity of NO is calculated by [64]:

$$(D_K)_{NO} = 9.7x10^3\ a\ (T/M_{NO})^{1/2} \quad \text{S5}$$

Where:

$D_{NO\text{-}N2}$ = Global diffusivity of NO into N_2 (cm^2/s)

$(D_K)_{NO}$= Knudsen diffusivity of NO into the catalyst pores (cm^2/s)

T = Temperature (K)

a = pore radius (cm)

M_{NO} = molecular weight of NO (g/mol)

M_{N2} = molecular weight of N_2 (g/mol)

Pt = Total Pressure (atm)

$\sigma^2_{NO\text{-}N2}$ = Lennard-Jones constant of potential energy (Å)[64]

$\Omega_{NO\text{-}N2}$ = Collision integral which is function of $k_BT/\varepsilon_{NO\text{-}N2}$ [64], where: k_B = is the Boltzman constant = $1.38x10^{-23}$ (J/K), $\varepsilon_{NO\text{-}N2}$ = Lennard-Jones constant of potential energy for the NO and N_2.

Because in our catalysts there are no micropores, only pores between 30 to 70 Å (Table 1), the value of ε_μ is zero and the equation S2 simplifies to:

$$De = D_M\varepsilon_M^2 \quad \text{S6}$$

C_{as} = Concentration of the reagent on the surface of the catalyst (mol/cm^3)

$$C_{as} = C_{ab} - [(-r_a)(\mu/\varrho\ D_{NO\text{-}N2})^{2/3}/a_t\ (G/\varrho)\ J_D \quad \text{S7}$$

$$J_D = 0.458/\varepsilon_B\ (d_p\ G/\mu)^{-0.407} \quad \text{S8}$$

$$\mu = 2.6693x\ 10^{-6}\ (M_{N2}T)^{0.5}/\ \sigma^2\ \Omega_\mu \qquad [65] \quad \text{S9}$$

Were:

C_{ab} = Concentration of NO in the gas phase (mol/cm^3) = $1.841x10^{-8}$ mol_{NO}/cm^3

μ = Gas viscosity

ϱ = Gas density

a_t = external area of the catalytic granules (cm^2/g) ($a_t = 6/d_p\ \varrho_p$)

ϱ_p = Particle density (g/cm^3)

G = Surface mass velocity ($g/s\ cm^2$)

d_p = Diameter of the catalytic particle sphere-shaped (cm) = 0.0148 cm

ε_B = Void space fraction of the intragranular space (in the catalytic bed)

σ = Collision diameter (Å)

Ω_μ = Collision integral

$-r_a = Q\ C_{ab}\ (Xa)/W$ = Reaction rate ($mol/g_c.s$) S10

Q = volumetric flow (cm^3/s)

C_{ab} = Concentration of NO in the gaseous phase (mol/cm^3), calculated using the equation of ideal gas.

$C_{ab} = P_{NO}/R_gT$

P_{NO} = Partial pressure of NO (atm)

T = Gas temperature in the reactor (K)

R_g = Gas constant

Xa = NO conversion

W = Catalyst weight (g)

The experimental and calculated values are shown in Table S1.

Table S1. Microreactor operating conditions to evaluate the SCR of NO at 250°C (average temperature).

Property name (units)	Experimental or calculated value
$-r_a$ = Reaction rate ($mol/g_c.s$)	4.10×10^{-7} (NO conv.= 50%)
ϱ_c = Catalyst granule density (g_c/cm^3)	0.417
R = Radius of the particle (cm)	$7.45x10^{-3}$
μ = N_2 gas viscosity (Pa.s) (250°C) [65]	$2.6x10^{-5}$
Xa = NO conversion	0.5
d_p = Diameter of the catalytic particle sphere-shaped (cm)	0.0148 cm
C_{ab} = Concentration of NO in the gas phase (mol/cm^3)	$1.841x10^{-8}$
C_{as} = Concentration of NO on the surface of the catalyst (mol/cm^3) (using the Ec.S7)	1.826×10^{-8}
D_{NO-N2} = Gaseous diffusivity of NO in N_2 (cm^2/s) (T = 250°C) From Chapman-Enskog equation.	0.603
D_K = Knudsen diffusivity (cm^2/s), (T = 250°C)	0.0133
D = Combined diffusivity (cm^2/s)	0.013
De = Effective diffusivity (cm^2/s) (Ec. S6)	0.00483
ε_M = Porosity in the in the macropore region	0.61
ε_μ = Porosity in the in the micropore region	0
T = Gas temperature in the reactor (K)	523
Pt = Total Pressure (atm)	1
a = pore radius (cm)	$3.3x10^{-7}$
M_{NO} = molecular weight of NO (g/mol)	30
M_{N2} = molecular weight of N_2 (g/mol)	28
ϱ = Gas density (g/cm^3)	0.001145

a_t = external area of the catalytic granules (cm^2/g)	579
ε_B = Void space fraction of the intragranular space (in the catalytic bed)	0.43
ϱ_P = Particle density (g/cm^3)	0.695
Q = volumetric flow (cm^3/s)	6.667
G = Surface mass velocity ($g/s\ cm^2$)	$9.719x10^{-3}$
P_{NO} = Partial pressure of NO (atm)	$4.5x10^{-4}$ atm
W = Catalyst weight (g)	0.15
Rg = Gas constant (cm^3 atm/mol K)	*82*
σ = Collision diameter (Å)	3.798
Ω_μ = Collision integral	0.86
C_{WP} (Value evaluated at 250°C and 1 atm)	**0.37**

References

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