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The total oxidation of propane over supported Cu and Ce oxides: A comparison of single and binary metal oxides

Philippe M. Heynderickx [a], Joris W. Thybaut [a,*], Hilde Poelman [a], Dirk Poelman [b], Guy B. Marin [a]

[a] *Laboratory for Chemical Technology, Department of Chemical Engineering, Ghent University, Krijgslaan 281 (S5), Ghent B-9000, Belgium*
[b] *Department of Solid State Sciences, LumiLab, Ghent University, Krijgslaan 281 (S1), Ghent B-9000, Belgium*

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ABSTRACT

The total oxidation of propane is studied by means of steady-state experiments over a set of Cu- and Ce-based catalysts at a propane inlet partial pressure of 0.6 kPa, an oxygen partial pressure of 3.5 kPa and temperatures from 595 to 648 K. The catalysts were characterized by inductively coupled plasma (ICP), Brunauer–Emmett–Teller specific surface area (BET), temperature-programmed desorption (TPD), X-ray diffraction (XRD), pulse reduction–reoxidation, and H_2- and C_3H_8-temperature-programmed reduction (TPR). A synergistic effect between cupric oxide, CuO, and ceria, CeO_2, is observed using a Mars–van Krevelen model to describe the kinetic data: the activation energies for reduction and reoxidation, obtained on the binary metal oxide catalyst with both cupric oxide and ceria, are 20 kJ mol^{-1} lower than those obtained on the single Cu- or Ce-based catalysts. The corresponding turnover frequencies are the highest.

1. Introduction

Nowadays, hydrocarbon emissions from both stationary and non-stationary sources are subjected to strict legislation. Catalytic oxidation offers the advantage that volatile organic component (VOC) can be removed from effluent streams with low VOC concentration at relative low temperatures [1]. Metal oxide catalysts offer a range of technical and commercial advantages that make them a viable alternative to noble metals. Long lifetime, poisoning and masking tolerance, capability of regeneration, availability in a large variety of metal oxide compositions, shapes and sizes, and low price lay the foundation for successful applications [2].

Cupric oxide is known to give highly active catalysts in total oxidation reactions [3–5]. The catalytic properties of the supported cupric oxide-based catalysts are enhanced by the addition of ceria [6,7]. The effect of the preparation method of Cu- and Ce-based catalytic systems on the activity has been intensively studied [8,9]. Nevertheless, up to now, no systematic investigation including catalytic activity and kinetics has been performed. The present paper applies inductively coupled plasma (ICP), Brunauer–Emmett–Teller specific surface area (BET), temperature-programmed desorption (TPD) and X-ray diffraction (XRD) in order to characterize three Cu- and Ce-based catalysts, prepared by the wet impregnation technique. Next to these physical characterizations, pulse reduction–reoxidation experiments, H_2- and C_3H_8-temperature-programmed reduction (TPR) experiments and catalytic steady-state experiments in propane total oxidation are performed to relate physical, catalytic and kinetic properties.

2. Procedures

2.1. Catalysts

Three commercial catalysts are used, see Table 1: a $CuO–CeO_2/\gamma-Al_2O_3$ catalyst synthesized by impregnation [10,11] with precursors $Cu(NO_3)_2$ and $Ce(NO_3)_4$ on a $\gamma-Al_2O_3$ support, denoted as CuCeO. Catalyst CuO is obtained by impregnation of $\theta-Al_2O_3$ with $Cu(NO_3)_2$. Further, a catalyst with pure ceria, denoted as CeO, is obtained by impregnation of a $\gamma-Al_2O_3$ support, with a lower surface area than the latter, with $Ce(NO_3)_4$.

2.2. Catalyst characterization

The bulk chemical composition of the tested catalysts was determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Advantage system, Thermo Jarrell Ash). N_2 physisorption at 77 K is applied to determine the BET specific surface area using a Gemini V (Micromeritics) automated system. BET values with their 95% confidence intervals were obtained by regression of the experimental data in the range $0.05 < p/p^0 < 0.30$ with the linear BET equation [12]. The catalyst's

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* Corresponding author. Fax: +32 (0) 9 264 49 99.
E-mail address: Joris.Thybaut@UGent.be (J.W. Thybaut).

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Nomenclature

Roman symbols

$a_{\beta^*,i}$	constant in Eq. (1) (mol s^{-1})
A	constant in Eq. (5) ($mol_{C_3H_8}$ $mol^{-1}_{C_3H_8,0}$)
A	preexponential factor, used in Eq. (2) (s^{-1})
A_i	surface area of the peak of component i (V s)
B	constant in Eq. (5) ($mol_{C_3H_8,0}$ $kg^{-1}_{cat}s^{-1}$)
C_i	concentration of adsorbed moles for component i (mol_i kg^{-1}_{cat})
C_O	oxygen storage capacity (mol_O kg^{-1}_{cat})
C_t	total concentration of active sites (mol kg^{-1}_{cat})
d_i	calibration factor for component i (V s mol^{-1})
D	dispersion (mol mol^{-1})
E	activation energy (kJ mol^{-1})
F_i	molar flow of component i (mol_i s^{-1})
h	Planck constant (J s)
$k_{app,0}$	initial apparent rate coefficient, see Eq. (7) ($mol_{C_3H_8}$ kg^{-1}_{cat} s^{-1} $kPa^{-n_{C_3H_8}-n_{O_2}}$)
k_B	Boltzmann constant (J K^{-1})
$k_{C_3H_8}$	reduction rate coefficient, see Eq. (S-13) ($mol_{C_3H_8}$ kg^{-1}_{cat} kPa^{-1})
k_{O_2}	reoxidation rate coefficient, see Eq. (S-14) (mol_{O_2} kg^{-1}_{cat} s^{-1} kPa^{-1})
K	shape factor, used in Eqs. (S-2) and (S-4) (–)
L	average particle size (nm)
M	molar mass (kg mol^{-1})
n	reaction order (–)
n_i	number of carbon atoms in component i (–)
Δn	change in number of moles (–)
N_C	number of carbon containing components (–)
p	partial pressure (kPa)
N_P	number of peaks in a TPR experiment (–)
r	specific reaction rate ($mol_{C_3H_8}$ kg^{-1}_{cat} s^{-1})
r_{col}	collision rate (mol $m^{-1}_{cat}s^{-1}$)
R	universal gas constant (kJ mol^{-1} K^{-1})
s	sticking probability (–)
$\Delta^{\neq}S^0$	standard activation entropy (J mol^{-1} K^{-1})
Δ_rS^0	standard reaction entropy (J mol^{-1} K^{-1})
S_0	initial molar amount of reducible substance (mol)
T	temperature (K)
TOF_0	initial turnover frequency ($mol_{C_3H_8}$ mol^{-1}_O s^{-1})
W_{cat}	catalyst mass (kg_{cat})
$X_{C_3H_8}$	propane conversion ($mol_{C_3H_8}$ $mol^{-1}_{C_3H_8,0}$)
y	mass percentage (kg kg^{-1})

Greek symbols

α_s	BET specific surface area (m^2_{cat} g^{-1}_{cat})
β	half-peak width, used in Eqs. (S-2) to (S-4) (–)
β^*	heating rate (K s^{-1})
ε	lattice distortion parameter (mm m^{-1})
ε	porosity (m^3 m^{-3})
θ	diffraction angle, used in Eqs. (S-2) to (S-4) (rad)
θ	fraction of active sites (–)
λ	X-ray wavelength (m)
Λ	TCD outlet signal, corrected for blank experiment (mol s^{-1})
ρ	density (kg m^{-3})
σ	standard deviation (dep.)
Ω	cross-section (m^2)

Subscripts

app	apparent
b	bed
cat	catalyst
i	component i
O^*	oxidized site
p	particle
0	initial, inlet
$*$	reduced site

Superscripts

0	standard
$*$	lumped
–	average
$\neq$	transition state

Abbreviations and acronyms

BET	Brunauer, Emmett and Teller
ICP	inductively coupled plasma
MVK	Mars-van Krevelen
OSC	oxygen storage capacity
TCD	thermal conductivity detector
TOF	turnover frequency
TPD	temperature-programmed desorption
TPR	temperature-programmed reduction
VOC	volatile organic component
XRD	X-ray diffraction

oxygen storage capacity (OSC), C_O, is determined by pulse chemisorption experiments using a Micromeritics AutoChem 2920. Temperature-programmed desorption (TPD) analysis has been performed in a Micromeritics AutoChem 2920. Sorptive molecules are carbon dioxide, carbon monoxide and oxygen. Carbon dioxide was used to measure the basicity of the catalysts. Propane and oxygen are used as probe because they are reactants [13].

Crystallographic analyses for the tested catalysts were performed by means of X-ray diffraction (XRD) measurements in θ–2θ mode using a Bruker-AXS D8 Discover apparatus with lynx eye detector covering 3° and 192 channels over the range 15–85° with a step of 0.04°. For evaluations of the average particle size, (L), and the lattice distortion, (ε), the Scherrer equation [14] and the Williamson–Hall equation [15] were applied on XRD experimental data, with correction for the instrumental width using a LaB_6 measurement. Next to the three catalysts, as received, structural characterization on six additionally treated samples is performed: all catalysts are reduced up to 923 K under a flow of 0.05 mol mol^{-1} H_2 in Ar and a total molar flow rate of 4.5×10^{-5} mol s^{-1} at 10 K min^{-1}. CuCeO is additionally reduced up to 623 and 1323 K. Finally, CuCeO is examined, which has been extensively used during 6000 h in propane total oxidation conditions [16]. Table 3 lists all tested catalysts with the corresponding reduction treatment.

Experimental details of the characterization techniques can be found in Supplementary content.

The determination of the particle porosity and the particle density is described in Supplementary content, see Sections S.8 and S.9.

2.3. Temperature-programmed reduction

H_2-TPR experiments are performed at heating rates of 2.5, 5.0, 7.5, 10.0, 15.0, 20.0 and 25.0 K min^{-1} up to 973 K under a flow of 0.05 mol mol^{-1} H_2 in Ar using 100 mg of catalyst material and a total molar flow rate of 4.5×10^{-5} mol s^{-1}. H_2-TPR experiments on the support material are performed at a heating rate of 10 K min^{-1}.