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Toluene total oxidation over $CuO-CeO_2/Al_2O_3$ catalyst: nature and role of oxygen species

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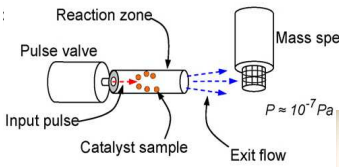
Introduction

Increasing interest is being shown in catalytic combustion processes, which are convenient ways for the prevention of emission as well as clean-up processes. Among the different emissions contributing to the damage of our environment, volatile organic compounds are a major source of direct (toxicity, odor) or indirect (“smog”) pollution of air.

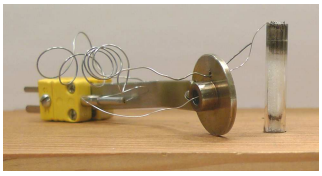
Objectives

- Study of the total oxidation of toluene on the $CuO-CeO_2/Al_2O_3$ catalysts using transient experiments
- Elucidate the participation of surface lattice oxygen during total oxidation
- Gain an understanding of the toluene total oxidation mechanism

Experimental

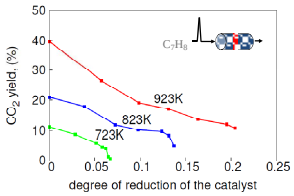


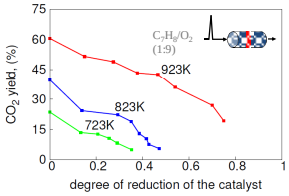
$CuO\ CeO_2/Al_2O_3$



Results

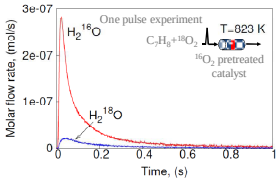
Toluene conversion to CO_2 in the presence and absence of O_2 in the feed mixture





- Mars and Van Krevelen type redox mechanism - proceeds through nucleophilic attack of the lattice oxygen of the oxides.
- Reaction rate decreases with degree of reduction of the catalyst and increases with amount of O_2 in the feed.

Oxygen isotopic exchange experiments

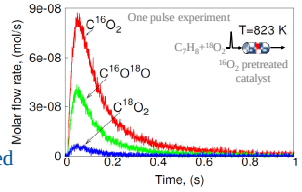


- $s + \square + {}^{18}O_2$ ----> ${}^{18}O_L{}^s + {}^{18}O_s$
- ${}^{18}O_s + \square$ ----> $s + {}^{18}O_L{}^s$
- $\square + {}^{16}O_L{}^b$ ----> ${}^{16}O_L + \square_b$

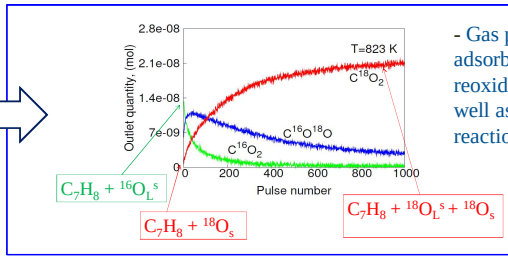
-%^{18}O in CO_2 is about 2 times that in H_2O

O species taking part in reaction

- ^{16}O at the surface lattice
- adsorbed ^{18}O
- ^{18}O moved to vacant lattice site



-Almost 10% of water formed constituted $H_2{}^{18}O$



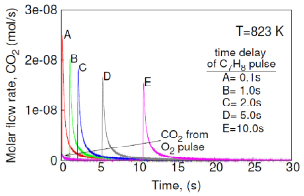
- Gas phase oxygen adsorbs on the surface-reoxidises the catalyst as well as takes part in the reaction

Role of adsorbed oxygen species

Alternating Pulse experiment

pump O_2 → CO_2

probe C_7H_8

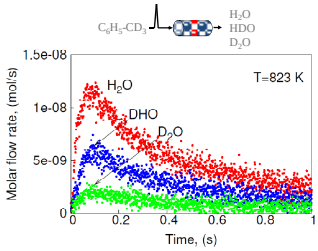


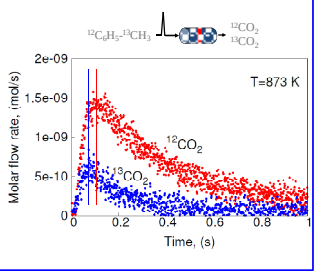
-CO_2 formed during the O_2 pulse was constant

-CO_2 pulse formed during the C_7H_8 pulse varied in size until time delay of C_7H_8 pulse =5s

-Weakly adsorbed oxygen species of lifetime < 1s

Isotopic labeling experiments





Conclusions

- Reaction occurs through Mars-van Krevelen mechanism.
- The adsorbed oxygen species also takes part in the reaction
- Oxygen species on the surface is highly reactive and have short life time
- Abstraction of C-H bonds takes place first followed by the C-C bonds.
- Carbon from the methyl group reacts first followed by the carbon from the phenyl group.