CO_2 Purification of Industrial Flue Gas: The Role of Copper and Carbonate Species in the Selective Catalytic Reduction Process.

Abou Rahhal A.[1], Genty E.[1], Cousin R.[1], Ponchel A.[2], Noel S.[2], Poupin C.[1], Siffert S.[1]*
[1]*Univ. Littoral Côte d'Opale, UR 4492, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, F-59140, Dunkerque, France*
[2]*Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), rue Jean Souvraz, SP 18, 62300 Lens, France*
**stephane.siffert@univ-littoral.fr*

Significance and Relevance

The redox treatments performed for cobalt-copper based catalyst significantly enhanced the catalytic performance of the selective catalytic reduction (SCR) of industrial flue gas. Analytical techniques underlined that Cu^{2+}/Cu^{+} species and mono- and polydentate carbonates are key parameters for the catalytic efficiency and selectivity under oxidative and wet conditions. This work emphasizes the novel role of carbonate and copper species for enhancing SCR performance to offer a low-cost alternative to noble metal catalysts in the purification of CO_2.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis - Air cleaning and combustion.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent decades, environmental and human health have become a critical concern due to various atmospheric pollutants mainly greenhouse gases such as CO_2. Therefore, it is essential to minimize the amount of CO_2 released to the atmosphere by carbon capture facilities for either its utilization or storage[1]. Industrial flue gas is composed of various gases, primarily CO_2, combined with other pollutants mainly NO and CO that are harmful to environment and human, as well as oxygen and water vapor[2]. Consequently, and prior to CO_2 valorization, CO_2 purification is a crucial step to remove both NO and CO using selective catalytic reduction process based on the following reaction: $NO + CO \rightarrow CO_2 + \frac{1}{2} N_2$. Transition metal-based catalysts have shown competitive results compared to noble metals being less expensive[3]. In addition, recent study underlined the effect of various thermal gas treatments (Air, He, 1% CO/He, and CO_2) for copper-based catalysts revealing its impact on the catalytic activity of SCR process[4]. The aim of this study is to synthesize cost effective and efficient copper and cobalt based catalyst, emphasizing the role of various thermal gas treatments and its impact on NO SCR by CO of industrial flue gas under oxidative and wet conditions.

Materials and Methods

Cobalt-copper based layered double hydroxide structures were synthesized by precipitating respective amounts of metal nitrates over sodium carbonate solution maintaining a constant pH using sodium hydroxide. The solution was set to age (maturation step) under room temperature and then filtered, washed and dried to obtain CoCuAl LDH samples.

These samples were thermally treated under different gas atmosphere at 400 °C to obtain the respective mixed oxide (CoCuAl Air or CO_2 samples). Subsequent redox cycles (CO-O_2 or CO-CO_2) were performed to promote the formation of specific Cu active sites denoted as CoCuAl Air CO-O_2 for example. The redox treated samples were then characterized by various techniques including X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Catalytic tests were conducted in a continuous-flow reactor under simulated flue gas conditions (20.5% CO_2, 8.8% O_2, 8.2% H_2O, with 1300 ppm of CO and 500 ppm of NO) at temperatures ranging from 100 to 400 °C.

Results and Discussion

The redox treatment performed on CoCuAl mixed oxides demonstrated lower temperature of total CO oxidation at 240 and 260 °C (Figure 1). XRD analysis revealed crystallographic phases of CuO and Cu_2O species within redox treated samples that are responsible for the enhancement of CO oxidation. The $Co_4Cu_2Al_2$ Air R CO-O_2 sample showed enhanced NO reduction compared to the air treated sample reaching 31% of N_2 yield at 320 °C with the highest selectivity of 56% (Figure 1). When comparing NO reduction temperatures, both redox treated samples exhibited lower temperature of reduction compared to the air treated sample where TG and FTIR analysis confirmed the presence of mono and polydentate carbonates that play a primary role for NO reduction. Based on further characterization (XPS, Raman …), the relationship between catalytic activity and the role of copper and/or carbonate species will be clearly defined.

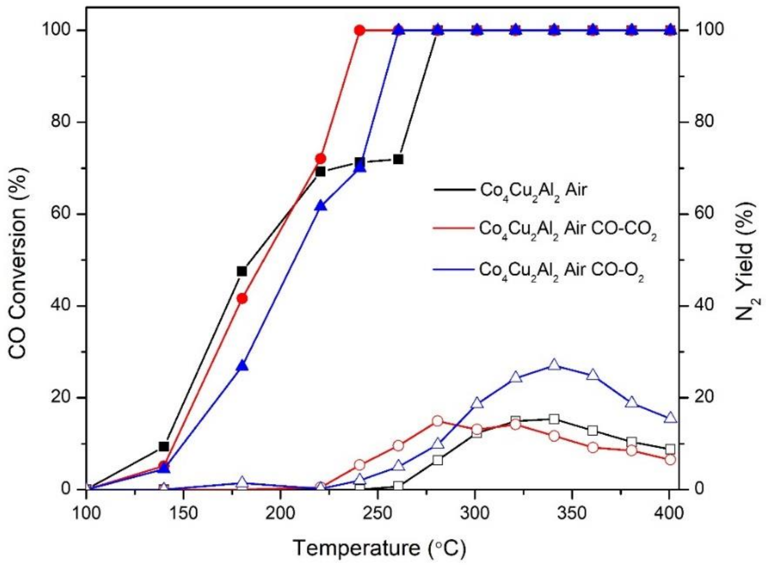

Figure 1. CO conversion and N_2 yield for $Co_4Cu_2Al_2$ air and subsequent redox treated samples as function of reaction temperature.

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