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TPD and TPSR study of CO interaction with CuO–CeO$_2$ catalysts

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ABSTRACT

The interaction of CO and CO$_2$ with CuO–CeO$_2$ catalysts, prepared by a citrate-hydrothermal method, has been studied employing the techniques of temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) of preadsorbed CO, as well as TPD of preadsorbed CO$_2$. The effect of copper content and activation temperature on the adsorptive behavior of the catalysts has been investigated. TPD studies of preadsorbed CO showed that a small fraction of CO is reversibly adsorbed, while most of it undergoes reaction with surface oxygen and desorbs as CO$_2$. Such profiles of CO$_2$ consist of a peak at 100–120 °C along with CO$_2$ desorption at high temperatures, which was significant for catalysts activated at 300 °C. TPSR of preadsorbed CO showed that reversibly adsorbed CO is highly reactive in the presence of gaseous oxygen. Catalytic sites, which form carbonates during interaction with CO, get eliminated with increase of catalyst activation temperature and do not contribute to the steady-state activity of the catalysts. The effect of CeO$_2$ appears to be mainly related to stabilization of highly dispersed copper oxide species and to creation of additional sites for CO adsorption and reaction, probably at the interface between the two oxides.

1. Introduction

The CuO–CeO$_2$ catalytic system has been studied by a large number of investigators in view of its application in (preferential) CO oxidation and many techniques have been employed for its characterization [1–34]. These include N$_2$O chemisorption, TPR, SEM, TEM, XRD, XPS, EXAFS, EPR and FTIR spectroscopy. On the other hand, temperature-programmed techniques, such as temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR), have been less often used to study the characteristics of CO adsorption on CuO–CeO$_2$. CO-TPD experiments over CuO–CeO$_2$ catalysts with CuO content up to 15 wt.% prepared by impregnation have been carried out by Luo et al. [14]. They found that almost no CO is desorbing from the catalysts and the TPD profile consists of a single CO$_2$ peak at 110 °C. Martinez-Arias et al. [4] have carried out CO-TPD for a 1 wt.% CuO/CeO$_2$ catalyst prepared by impregnation and activated at 500 °C. The reported TPD profiles consist of a small CO peak at 70–80 °C and a CO$_2$ peak at 110 °C with a tail extending up to 450 °C. Similar desorption behavior has been reported recently by Caputo et al. [33] during CO-TPD over a 4 wt.% CuO/CeO$_2$ catalyst prepared by impregnation. We have also reported on the adsorption and reaction of CO on combustion-synthesized CuO–CeO$_2$ catalysts [32]. Adsorption of CO was found to proceed through initial reduction of Cu^{2+} and formation of carbonate species followed by adsorption of CO on reduced Cu^{+} sites.

In the present work, we examine the interaction of CO with CuO–CeO$_2$ materials, prepared via a citrate-hydrothermal method, employing the techniques of TPD and TPSR of preadsorbed CO. TPD experiments of preadsorbed CO$_2$ were also carried out, as CO$_2$ is the reaction product between CO and O$_2$. The effect of copper content and activation temperature on the adsorptive behavior of the catalysts has been investigated. Physicochemical characterization and activity data in preferential CO oxidation of these catalysts have been reported in a previous publication [1].

2. Experimental

2.1. Preparation of catalysts

CuO–CeO$_2$ samples were prepared via a citrate-hydrothermal method [1]. Aqueous solutions of metal acetates – cerium acetate [Ce(C$_2$H$_3$O$_2$)$_3$·1.5H$_2$O] and copper acetate [Cu(C$_2$H$_3$O$_2$)$_2$·H$_2$O] – were mixed with an aqueous solution of citric acid under continuous stirring. The molar ratios of citric acid to each metal acetate were adjusted as citric acid/Ce = 1/1 and citric acid/Cu = 2/3. The mixed solution was treated hydrothermally in a stainless steel autoclave, at 150 °C (heating rate = 2 °C min^{-1}) for 24 h. Following

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hydrothermal treatment, the autoclave was opened, excess water was decanted and the remaining paste was dried for 12 h at 120 °C and subsequently activated at 300, 400 or 500 °C under a flowing 20% O_2/He mixture (20 $cm^3 min^{-1}$) for 2 h.

For comparison purposes, two additional catalysts, namely 7.5 wt.% CuO/CeO_2 and 7.5 wt.% CuO/Al_2O_3, were prepared by impregnation using an aqueous $Cu(NO_3)_2 \cdot 3H_2O$ solution of the desired concentration. The supports in this case were CeO_2 made via the hydrothermal-citrate method (S_{BET} = 27.6 $m^2 g^{-1}$) and commercial Al_2O_3 (Alfa-Aesar, S_{BET} = 90 $m^2 g^{-1}$). The samples were dried overnight in an oven at 120 °C and then activated at 400 °C under a flowing 20% O_2/He mixture (20 $cm^3 min^{-1}$) for 2 h.

All samples were sieved to obtain the desired fraction of particle diameter between 90 and 180 μm. For ease of reference, the catalysts are encoded as follows: *x*Cu-TTT, where *x* is the Cu/(Cu + Ce) atomic ratio and TTT is the activation temperature. For example, the catalyst 0.25Cu-400 was prepared at a ratio of Cu/(Cu + Ce) = 0.25 and was activated at 400 °C.

2.2. Temperature-programmed techniques (CO-TPD, CO_2-TPD and TPSR)

TPD and TPSR experiments were performed in a fixed-bed reactor system, described in detail elsewhere [5]. Prior to TPD, the catalyst (30–50 mg with particle size 90 μm < d_p < 180 μm) was treated at its activation temperature for 30 min under a 20% O_2/He flow (20 $cm^3 min^{-1}$), and cooled under the same gas flow to 32 °C. After purging with He, adsorption of CO (CO-TPD and TPSR) or CO_2 (CO_2-TPD) was carried out under a flow of 1% CO/He or 1.7% CO_2/He mixture, respectively. Following completion of the adsorption, as indicated by stable signals of CO or CO_2 in the mass spectrometer, the reactor was purged with pure He for ~10 min. Then, the TPD or TPSR run was started under a flow of 40 $cm^3 min^{-1}$ of He (CO-TPD and CO_2-TPD) or 1% O_2/He (TPSR-O_2) with a heating rate of 20 °C min^{-1} up to the corresponding activation temperature for each catalyst. This was followed by soak at this temperature until the MS signals returned to baseline levels. A mass spectrometer (Omnistar/Pfeiffer Vacuum) was used for on-line monitoring of effluent gases. Mass peaks of CO, CO_2, O_2, H_2 and H_2O were monitored during the experiments. The only products detected, in all cases, were CO and CO_2. CO (*m*/*z* 28) and CO_2 (*m*/*z* 44) signals were calibrated using gas mixtures prepared in situ and analyzed in a pre-calibrated gas chromatograph with a TC detector (Shimadzu 14B). The contribution of CO_2 to the *m*/*z* 28 signal was taken into account for the calculation of CO concentration.

3. Results

3.1. TPD of CO and CO_2

As stated in Section 2, the maximum temperature during TPD was the same as the corresponding activation temperature of the catalyst tested in the specific run. In the case of catalysts activated at 300 °C, for example, the TPD run consisted of a ramp of 20 °C min^{-1} to 300 °C, followed by soak at this temperature, until the signals returned to baseline levels. Typical TPD profiles along with the applied temperature program after CO adsorption at RT are shown in Fig. 1(a) and (b) for 0.50Cu–300 and 0.50Cu–400 catalysts, respectively. The majority of adsorbed CO desorbs as CO_2, but there is also molecular desorption of CO at low temperatures with a peak at 75 °C. CO desorption starts immediately upon initiation of the temperature ramp. The CO_2 profiles are characterized by a main peak at ~110 °C and a second peak above 300 °C, which is more intense for the 0.50Cu-300 sample.

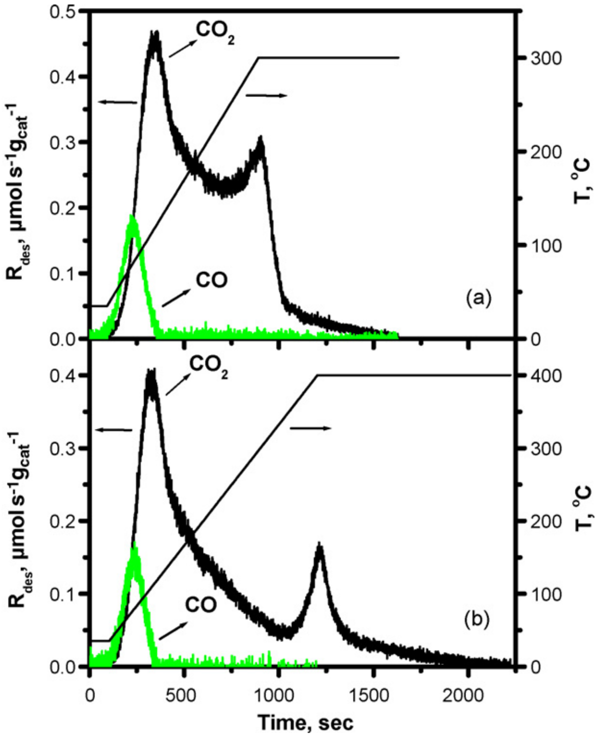

Fig. 1. CO and CO_2 TPD profiles along with the applied temperature program after CO adsorption at RT on 0.50Cu catalyst, activated at 300 °C (a) and 400 °C (b).

The effect of catalyst Cu content on the resulting TPD profiles of CO_2 following CO adsorption is depicted in Fig. 2(a)–(c) for catalysts activated at 300, 400 and 500 °C, respectively. The corresponding profiles of CuO and CeO_2 are also shown for comparison purposes. CO desorption profiles were similar in all cases to those shown in Fig. 1 and are not plotted for reasons of clarity. In the case of CeO_2, very small amounts of CO_2 and no CO were detected during TPD, with CO_2 appearing above 225 °C and slightly increasing with temperature. The CO_2 profile of pure CuO consisted of a small peak at ~100 °C with a tail extending up to 300 °C. Regarding CuO–CeO_2 catalysts, the profiles of 0.25Cu, 0.50Cu and 0.75Cu bear many similarities, while the behavior of 0.10Cu is significantly different: CO_2 desorption from the 0.10Cu-300 sample starts above 130 °C giving a broad peak at 200–250 °C compared to a peak at 120 °C for all other catalysts activated at 300 °C (Fig. 2(a)). The CO_2 profiles of catalysts activated at 400 °C (Fig. 2(b)) also indicate a gradual shift of the CO_2 peak to lower temperatures accompanied by an increase in the amount of desorbed CO_2 with increase of Cu content. When the activation temperature is 500 °C (Fig. 2(c)), the high-temperature CO_2 peak has diminished and the profiles are characterized by a peak at 100 °C (150 °C for 0.10Cu). Increase of catalyst activation temperature leads to a decrease of the amount of CO_2 desorbing from the catalysts. The high-temperature (HT) CO_2 desorption peak diminishes with increase of catalyst activation temperature: it is quite significant for the samples activated at 300 °C, but has essentially disappeared for catalysts activated at 500 °C. In addition, the intensity of the low-temperature (LT) CO_2 peak decreases by half. A small shift of the CO_2 peak temperature from 110–120 to 100 °C is also observed with increase of the catalyst activation temperature.

The quantities of desorbed CO_2 and CO (in μmol g^{-1}) and the specific adsorption capacity (in μmol m^{-2}) of the catalysts following adsorption of CO at RT are presented in Table 1 (calculation of specific adsorption capacities employed the specific surface areas, S_{BET}, of all catalysts, which are given in Table 2). The quantity of desorbed CO is 5–15% of the total (CO + CO_2) amount desorbed from