307b On the Selectivity of Cuo/Ceo2 Catalysts for the Preferential Oxidation of Co in H2-Rich Gases

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An essential requirement for the PEM fuel cell is to feed a gas mixture almost free from carbon monoxide, which is generally present as by-product of the hydrocarbon reforming processes. Actually, cell performances are severely affected by even traces of CO (upper limit at about 10 ppm). To date, the most promising technology for removing CO from H2 streams is the preferential catalytic oxidation of CO to CO_2 (CO-PROX) (Korotkikh, 2000), a process in which a catalyst selectively oxidizes up to about 1% CO oxidizing as small amount of the 30–70% H_2 as possible. In the preferential oxidation of CO, CuO/CeO_2 catalysts exhibit properties that make them very competitive with the most investigated systems. CuO/CeO_2 shows an activity higher than the Pt based catalysts and a very high selectivity, even higher than the gold based samples (Avgouropoulos, 2003; Liu, 2004). However it is still a matter of discussion about the origin of the high selectivity shown by these catalysts to selectively oxidize CO in presence of high H_2 concentrations, as well as about the active and selective copper species on catalyst surface and the reaction mechanism. CO and H_2 temperature programmed reduction tests (TPR) coupled with in-situ IR analyses and tests on the catalytic activity in the CO PROX reaction have been performed in order to investigate some of the aspects above illustrated The paper concerns with catalyst samples prepared by wet impregnation of commercial ceria supports in aqueous copper acetate solutions, dried at 120°C and calcined at 450°C for two hours. The materials were characterized by XRD, SEM, and spectrophotometric UV analyses (for measurements of Cu content). The activity tests were performed in conditions as close as possible to those of the practical interest for CO-PROX, feeding to the lab-scale reactor a mixture of 0.1-0.5vol% CO, 0.5-2vol% O2, 50vol% H_22, 0-15vol% CO_2 and 0-10vol% H_2O at a contact time of 0.01-0.05 $g{\bullet}s{\bullet}cm^{-3}$. MatLab Program has been used for the kinetic modeling in which, in the first approximation here presented, two power law kinetic equations for both CO and H_2 oxidation have been taken into account CO and H_2 oxidation activity tests, separately performed, showed that the catalyst investigated exhibit a lower light-off temperature and activation energy for CO than for H_2 oxidation, suggesting that such catalytic systems can be considered as intrinsically selective for CO PROX. Actually, CO PROX catalytic tests (i.e. the tests carried out by simultaneously feeding both reactants) seems the mere re-proposition of the two reactions of oxidations which seem to be not significantly influenced by the mutual presence. Performing kinetic measurements of CO PROX at constant temperature and different CO/H_2 ratios (or different contact time) has proved that the high selectivity of these catalysts is a unique function of temperature. The parameters identification estimated a value of about 20 kcal/mol for the activation energy of the oxidation of CO, while for the oxidation of H_2 the same parameter assumed a value of about 36 kcal/mol. This means that the high selectivity of such catalyst, which is also variable (decreasing) with increasing temperature, so giving raise to the maximum of CO conversion can be explained by the different dependence of the reaction rate on temperature, since CO oxidation is faster at low temperature but grows in a slower way, if compared to the oxidation of hydrogen. Moreover, we experimentally proved that the presence of a maximum of CO conversion with increasing temperature is not attributable to the proceeding of the reverse WGS reaction (as was instead observed for noble metal catalysts). These observations all agree with the kinetic model that estimates for CO a reaction order variable with temperature from about 0.7 in the low temperature region up to about 1.3 at the highest temperatures investigated. On the other hand, the reaction order for oxygen in good agreement with the experimental evidences (where no significant variation is observed neither for the conversion nor for the selectivity by changing the O_2/CO ratio), was estimated to be nearly zero for both reactions: about 0.003 for the oxidation of CO and slightly higher (0.18) for the oxidation of hydrogen. The investigation over catalysts with variable copper content evidenced that the activity and the selectivity to oxidize preferentially CO in presence of H_2 is optimal in correspondence to a concentration of 4.2wt% of CuO on ceria. Such a phenomenon has been studied by both TPR and FT-IR techniques, which allow us to conclude that while increasing the copper content up to the optimal value the concentration of the active species increases and could be tentatively attributed to a CuO microclusters strongly interacting with CeO_2. Above 5 wt% a segregation of bulk CuO particles occurs, as already visible in XRD spectra, whose species are unable to adsorb CO grows with negligible contribution to its conversion, but significant enhancement of the undesired oxidation reaction. Finally, over the CuO/CeO_2 catalyst investigated, the presence of carbon dioxide and water vapor in the H_2-containing gas does not significantly alter the catalyst performances, shifting the activity in a slightly higher temperature range still storing quite the same selectivity for the process. Reference Korotkikh O., Farrauto R., Catalysis Today , 2000, vol. 62, p.249-254 Avgouropoulos G., Ioannides T., Applied Catalysis, A, 2003, vol. 244, no.1, p. 155-167 Liu, Y.; Fu, Q.; Stephanopoulos, M. F., Catalysis Today 2004, vol. 93-95, p.241-246