Control of catalytic activity of Ag/CeO_2 catalysts tailoring $Ag–CeO_2$ interfacial interaction

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Abstract: Ag/CeO_2 catalysts were prepared by three different techniques (incipient impregnation, co-precipitation and impregnation of pre-reduced CeO_2) and tested in oxidation of ethanol, total oxidation of CO and soot combustion. The features of $Ag-CeO_2$ interaction were studied by TPR-H_2, TEM HR, XPS and Raman methods. It was shown that the use of co-precipitation technique led to strong interaction between silver and ceria particles as well as to the epitaxy of silver particles (d_{111} = 2.35 Å) on the CeO_2 surface (d_{111} = 3.1 Å). Strengthening of metal–support interaction enhanced catalytic activity in CO oxidation, soot combustion and selective oxidation of ethanol to acetaldehyde.
Keywords: Ag/CeO_2, metal–support interaction, low-temperature oxidation

1. Introduction

Metal–support interaction is one of the factors strongly affecting the catalytic activity and stability of noble metals supported on reducible oxides. An issue of great importance is how to control and tailor such interaction. The design of catalysts with controllable metal–support interface can be used as a powerful tool to enhance the catalytic activity in different reactions [1, 2]. Ag/CeO_2 are very promising catalysts for low-temperature oxidation of organic compounds such as formaldehyde, ethanol, CO, soot [3, 4]. Thus, the present work is focused on the design of Ag/CeO_2 catalysts with controllable $Ag–CeO_2$ interfacial interaction and on the effect of this interaction on the catalytic activity in ethanol oxidative dehydrogenation, CO oxidation and soot combustion.

2. Experimental

Ceria was prepared by precipitation of $Ce(NO_3)_3$ by ammonia at pH~10. To synthesize Ag/CeO_2 catalysts with controllable interfacial interaction, three preparation techniques were selected: incipient wetness impregnation (**Ag/CeO_2 (imp)**), impregnation of pre-reduced CeO_2 (**Ag/CeO_2 (red-imp)**) and co-precipitation (**$Ag-CeO_2$ (co-DP)**), which included a redox reaction between Ag(I) and Ce(III) to strengthen the interphase interaction between the metal and the support. N_2 adsorption/desorption, XRD, TPR-H_2 analysis, HR-TEM, XPS and Raman techniques were used to study the $Ag–CeO_2$ interaction and the influence of this interaction on the activity and selectivity of the Ag/CeO_2 catalysts in selective oxidation of ethanol, CO oxidation and soot combustion.

3. Results and discussion

Ceria with S_{BET} of 66 m^2/g and pore volume of 0.098 cm^3/g was used as a support. No significant changes in the pore size distribution of Ag/CeO_2 (imp) and Ag/CeO_2 (red-imp) catalysts were observed in comparison with the CeO_2 support. This finding suggested homogeneous distribution of silver on the support surface that was confirmed by XRD (absence of reflexes of Ag and Ag_2O phases). Small silver clusters weakly bonded to CeO_2 were detected by HR-TEM for the Ag/CeO_2 (imp) catalyst, small Ag particles homogeneously distributed over ceria were found as well for the (red-imp) catalyst.

Conversely in the case of Ag/CeO_2 (co-DP) catalyst, the S_{BET} and pore volume were smaller in comparison with CeO_2. This may be caused by the interaction of silver precursors with the support during the synthesis. According to XRD and TEM data, the mean crystallite size of CeO_2 was 11-14 nm, Ag particle size being <5 nm. A decrease in cell parameter of ceria in the Ag/CeO_2 (co-DP), as calculated by XRD data, indicated an increase of the number of oxygen vacancies in the structure of CeO_2 due to the presence of silver. The occurrence of a strong metal–support interaction for this catalyst was further supported by HR-TEM micrographs where the epitaxy of silver particles on ceria was detected. XPS analysis detected silver in metallic state with higher Ag surface concentration for both the impregnated catalysts, Ag/CeO_2 (imp) and (red-imp) with respect to the co-DP.

Raman results pointed out to higher amount of oxygen vacancies for the catalysts Ag/CeO_2 (co-DP) and Ag/CeO_2 (red-imp). TPR data confirmed the enhanced Ag-CeO_2 interaction in such catalysts.

Strong metal–support interaction increased the activity in the oxidative dehydrogenation of ethanol for Ag/CeO_2 (co-DP) in comparison with Ag/CeO_2 (imp) and CeO_2. As shown in Fig. 1a, 15% ethanol conversion with 100% selectivity towards acetaldehyde was reached at 85 °C over Ag/CeO_2 (co-DP) catalyst. Above 130 °C, the deep oxidation of ethanol to CO_2 becomes the predominant reaction. The testing of catalysts in CO oxidation showed that CO conversion started at room temperature. CO conversion up to 20% had similar behavior for all catalysts. Activation energies calculated for conversion (X) from 4 (4.5)% up to 20% were 29.3 kJ/mol, 30.5 kJ/mol and 42.6 kJ/mol for Ag/CeO_2 (co-DP), Ag/CeO_2 (red-imp) and Ag/CeO_2 (imp), respectively, see Fig. 1b. To study catalytic activity of the samples in soot oxidation the simultaneous thermal analysis (STA-TGA) was used. Soot oxidation over Ag/CeO_2 catalysts was observed in a temperature range of 230-640 °C. The activity increased in the order Ag/CeO_2 (imp) (T_{max} = 460 °C) < Ag/CeO_2 (co-DP) (T_{max} = 415 °C) < Ag/CeO_2 (red-imp) (T_{max} = 390 °C) (see Fig. 1c). According with the so far reported results, a good relationship between Ag–CeO_2 interaction and catalytic activity was revealed.

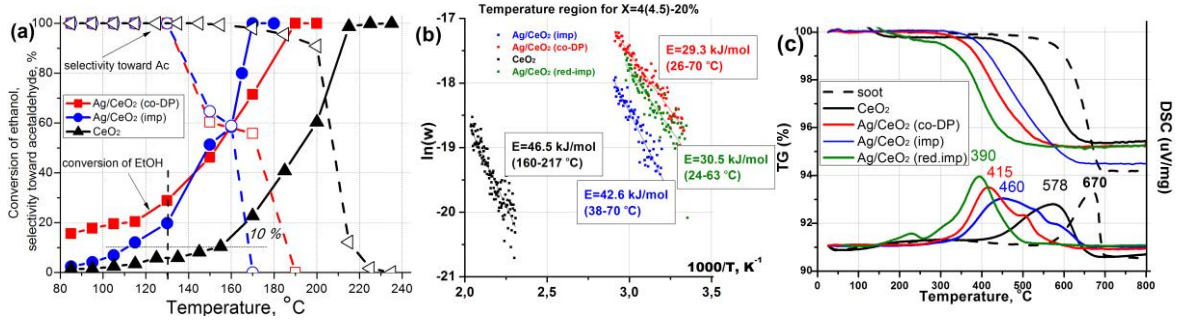

Figure 1. Catalytic properties of samples in oxidative dehydrogenation of ethanol (a), CO oxidation (b) and soot combustion (c)

4. Conclusions

The control of the Ag–CeO_2 interfacial interaction plays a crucial role in development of highly effective silver-containing catalysts for both selective and total oxidation of organic compounds. The redox reaction between Ce(III) and Ag^+ during co-deposition and impregnation is an effective way to enhance the interfacial interaction and improve the catalytic properties. Thus, stronger Ag–CeO_2 interaction increases the reducibility and oxygen vacancies content of ceria with an improved activity of Ag/CeO_2 catalysts in oxidative dehydrogenation of ethanol to acetaldehyde, low-temperature CO oxidation and soot combustion.

References

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