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Hysteresis phenomenon in CO and hydrogen oxidation on Cu–Ce–Zr–O systems

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Hysteresis phenomenon in CO and hydrogen oxidation on the CuO/$Ce_{0.7}Zr_{0.3}O_2$ systems is mainly caused by changing their states because of reduction and destruction of a Cu–Ce–Zr–O solid solution obtained during the preparation of catalysts by the decomposition of starting metal nitrates.

Ceria-based catalysts doped with transition metals are widely used in redox processes.[1,2] Copper-containing systems like Cu–Ce–M–O (M = Zr, La or Sm) are of interest because of their high activity in CO oxidation at relatively low temperatures (60–180 °C).[3–5] This property makes these systems promising for removing CO from H_2-containing mixtures in fuel cells.

We found a temperature hysteresis of the activity of CuO/$Ce_{0.7}Zr_{0.3}O_2$ catalysts in CO oxidation in an excess of H_2. The dependence of the width of a hysteresis loop on the composition of the catalysts and their treatment conditions is difficult to explain by a local overheating of the catalyst surface[6] or by a steady-state multiplicity of the reacting system.[7,8]

The (0.5–80.0%)CuO/$Ce_{0.7}Zr_{0.3}O_2$ catalysts were prepared from $Cu(NO_3)_2{\cdot}3H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$ salts by their simultaneous decomposition (evaporation of aqueous solutions and drying at 100–120 °C for 1 h; calcination in air at 300 °C for 2 h). Catalytic measurements were carried out in a flow microreactor (quartz tube with an internal diameter of 6 mm) at atmospheric pressure on 0.05 g of catalyst powder (particle size < 0.3 mm) diluted with 0.05 g of quartz grit (0.1–0.3 mm). The reaction mixture consisted of CO (2 vol%), O_2 (1 vol%), N_2 as an internal standard (4 vol%), H_2 (46 vol%) and He (47 vol%). The GHSV was 35 000 h^{-1} in all experiments. The reactor was heated at a rate of 2 K min^{-1} with stops in every 20 °C for 30 min for the chromatographic analysis of the reaction mixture. Temperature (T) was increased up to a level when the total O_2 conversion was achieved. After that the reactor was cooled in an analogous temperature regime. The error in the estimation of CO and O_2 conversions did not exceed 5 rel%. The temperature-programmed reduction (TPR) of catalysts (0.02 g) after different pretreatments was performed in the stream of 10% H_2 + 90% Ar (30 cc min^{-1}) at a heating rate of 20 K min^{-1}. The XRD spectra of powder samples were obtained on a DRON-3M diffractometer with CuKα radiation (Ni filter, $\lambda = 0.15407$ nm) in the angle range 2θ 5–75°.

We observed the hysteresis phenomenon in all of the test (0.5–80%) CuO/$Ce_{0.7}Zr_{0.3}O_2$ systems. The value of this effect depends on the pretreatment conditions of the catalysts and on CuO concentration ([CuO]) in a complicated way. In the case of fresh samples, the conversions of CO [K(CO)] and oxygen [$K(O_2)$] are noticeably lower with increasing temperature than those obtained at a cooling stage of catalysts. The hysteresis effect determined from the width of a hysteresis loop at an O_2 conversion of 50–80% (ΔT_{50-80}) is in the range 25–60 °C for samples containing 0.5–5.0% CuO. An increase in [CuO] in the catalyst results in a decrease in ΔT_{50-80} to 10–20 °C. Note that the activity of catalysts increases with [CuO] loading. For example, at 120 °C, $K(O_2)$ and K(CO) determined on cooling the catalyst increased from 2.4 to 89 and from 1.9 to 60%, respectively, with increasing CuO content of the catalysts from 0.5 to 20%.

The influence of pretreatment conditions on a hysteresis loop can be seen from the temperature dependence of $K(O_2)$ and K(CO) in the range 100–280 °C for a sample of 0.5% CuO/$Ce_{0.7}Zr_{0.3}O_2$ in a series of consecutive experiments [Figure 1(*a*)–(*c*)]. In all cases, the conversions of CO and O_2 on cooling are essentially higher than those during the heating of the catalyst. Thus, $K(O_2)$ does not reach 8% during the heating of a fresh sample to 200 °C, whereas $K(O_2)$ is ~25% on cooling of the catalyst [Figure 1(*a*)]. The value of ΔT_{50-80} exceeds 25 °C in the temperature range 220–240 °C. It was found that the effect of hysteresis was substantially weakened in a repeated test [Figure 1(*b*)]: ΔT_{50-80} is about 10 °C. The hysteresis effect increases slightly if the catalyst was pretreated in air at 300 °C for 1 h [Figure 1(*c*)]. For example, ΔT_{80} was ~1.5 times higher than the corresponding value determined in a previous test [Figure 1(*b*)]. The above data demonstrate the dependence of the hysteresis phenomenon on both the composition of test catalysts and the pretreatment conditions.

Considering the contribution of possible overheating of a 0.5% CuO/$Ce_{0.7}Zr_{0.3}O_2$ catalyst to the hysteresis of its activity, it is necessary to take into consideration the relatively low caloricity of the reaction mixture used (1% O_2), which designates the thermal effect of the reaction. According to Subbotin *et al.*,[6] a decrease in the CO content of the mixture from 14.2 to 6.2%

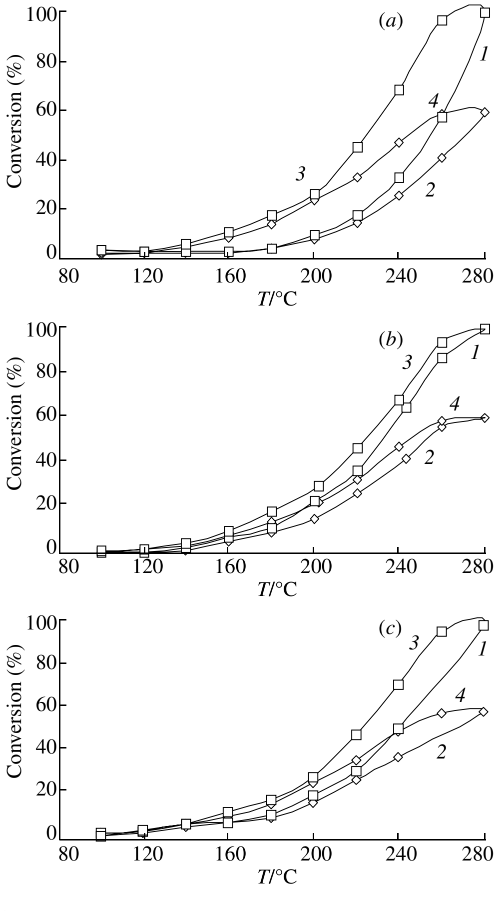

Figure 1 Conversions of O_2 (*1*, *3*) and CO (*2*, *4*) *vs*. temperature on (*1*, *2*) heating or (*3*, *4*) cooling a 0.5% CuO/$Ce_{0.7}Zr_{0.3}O_2$: (*a*) a fresh sample, (*b*) a repeated run (after cooling the catalyst in a reaction mixture to 60 °C), (*c*) a run after (*a*), (*b*) and catalyst treatment at 300 °C in air for 1 h.

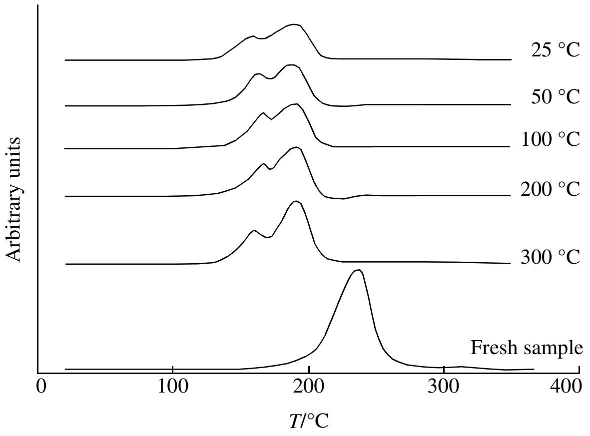

Figure 2 TPR spectra of a fresh 7.5% $CuO/Ce_{0.7}Zr_{0.3}O_2$ catalyst and a reoxidised catalyst at various temperatures. After TPR, the catalyst temperature was decreased in Ar to 300, 200, 100, 50 or 25 °C, at which the sample was oxidised in an air flow (30 $cm^3\ min^{-1}$).

with a stoichiometric excess of O_2 results in the narrowing of a hysteresis loop by a factor of about 6. The estimate of heat transfer on a catalyst particle and in the catalyst – gas phase – reactor wall system using the criteria[9,10] shows that under our conditions (reactor diameter and catalyst particle size) the thermal effect does not cause a noticeable overheating of the catalyst layer. Changes in the catalyst states are most probably responsible for the observed dependence of the temperature hysteresis on the pretreatment conditions and sample composition. The TPR results confirm these observations. For example, the TPR curve of a fresh 7.5% $CuO/Ce_{0.7}Zr_{0.3}O_2$ sample has one peak with a maximum near 235 °C. However, two peaks with maxima at lower temperatures (160 and 185 °C) appeared after the reoxidation of this sample at 300 °C. The two-stage reduction is most typical of CuO-containing samples.[11,12] The shapes and positions of peaks in TPR spectra were almost not changed in the following redox cycles. Note that the H_2/Cu molar ratio determined for a fresh sample is 1.9. However, this value decreased almost twice ($H_2/Cu = 1$) in the tests with a reoxidised catalyst at 300 °C. The results can be explained by the fact that the fresh catalyst represents a solid solution containing Ce^{4+}–O–Cu^{2+}–O–Ce^{4+} fragments, the reduction of which results in the formation of Cu^0 and Ce^{3+}. The reduction of an oxide matrix was also noticed for the $CuCe(La)O_2$ system prepared by precipitation.[13] The reoxidation of reduced Cu–Ce–Zr–O samples causes the formation of CuO particles located on the surface of the $Ce_{0.7}Zr_{0.3}O_2$ support (the H_2/Cu ratio was no higher than unity).

The formation of a Cu–Ce–Zr–O solid solution during catalyst preparation is confirmed by XRD data. The cell parameter of a mixed Ce–Zr oxide decreases from 0.5403 to 0.5375 nm with increasing [CuO] to 20%. This fact indicates the penetration of Cu^{2+} ions into the Ce–Zr–O structure because the ionic radius of Cu^{2+} (0.079 nm) is noticeably lower than the radius of Ce^{4+} (0.102 nm). The solid solution formed was also observed in the CuO/CeO_2 system,[9] where the cell parameter decreased with increasing [CuO] to 15%. Interestingly, the CuO phase was not detected by XRD in the 20% $CuO/Ce_{0.7}Zr_{0.3}O_2$ sample even after reduction in hydrogen at 300 °C followed by reoxidation in air at room temperature for several hours. This fact indicates the formation of an amorphous phase of CuO on the surface of the $Ce_{0.7}Zr_{0.3}O_2$ support.

Thus, the solid solution of oxides is formed during the preparation of $CuO/Ce_{0.7}Zr_{0.3}O_2$ catalysts by the simultaneous decomposition of metal nitrates. This solution is destructed during the reduction of Cu^{2+} with the formation of fine copper particles on the support surface. As a consequence, wide hysteresis loops appeared on testing the fresh catalysts. The quantity of CuO localised on the surface of the Cu–Ce–Zr–O solid solution increases with copper concentration in catalysts. The reduction of surface CuO species occurs at lowered temperatures to weaken the hysteresis effect for fresh samples. On the other hand, the conditions of catalyst reoxidation influence the width of the hysteresis loop to some extent. The deep oxidation of copper widens the hysteresis loop, which reflects active centre formation at the repeated use of catalysts.

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