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Synergy of $Fe_xCe_{1-x}O_2$ mixed oxides for N_2O decomposition

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Abstract

Fe–Ce mixed oxides prepared by coprecipitation showed considerable synergy in N_2O decomposition when compared with pure metal oxide counterparts. The mixed system also displayed higher stability in reaction at high temperature. Through characterisation by XRD, XPS and TPR, the activity–stability improvement is ascribed to the formation of Fe-doped ceria and Ce-doped hematite and also to increased surface area. The intimate interaction in the mixed phases results in easier reduction. Thus the release of oxygen, which is the rate-determining step in this N_2O decomposition, becomes more facile.

Keywords: Ceria; Iron catalysts; Co-precipitation; Hematite; N_2O decomposition

1. Introduction

Ceria-based catalysts display a wide range of applications, including vehicle exhaust gas emission control, electrolytes for solid oxide fuel cells (SOFCs), and catalysts for various oxidation and hydrogenation reactions [1–3]. For most of these applications, ceria-based oxides act as promoters of the active ingredient (or metal oxides) with which they are in close contact [1]. Depending on the type of reaction and the experimental conditions, different promoting effects, including structural, redox states, and bifunctional promotion, have been proposed to account for the synergetic effects observed [1]. Ceria-based mixed oxides $(Ce_xM_{1-x})O$ are versatile solid oxygen exchangers. At temperatures in the range of 400–800 °C, the redox couple $Ce^{IV} \leftrightarrow Ce^{III}$ facilitates oxygen storage and release from its bulk fluorite lattice, making it an ideal candidate for catalytic and/or electrocatalytic oxidation applications in SOFCs [3]. However, the *surface* redox chemistry of ceria is sensitive even at low temperatures to crystal structure defects [4], which can be tuned by substituting some of the Ce cations with ions of different sizes and/or charges [5]. Substitution of a lower-valent metal ion (e.g., M^{III}) by cerium lowers the energy barrier for oxygen migration [6]. However, smaller homovalent ions (Zr^{IV}) enhance the oxygen storage capacity (OSC) by decreasing the activation energy for the reduction ($Ce^{IV} \rightarrow Ce^{III}$) and retarding OSC degradation at high temperature. Given the effects of trivalent ions and smaller sizes on the structure and properties [7,8], there is considerable scientific interest in introducing M^{III} ions into the ceria lattice.

Ceramic methods allow the formation of such solid solutions, but the preparation temperature and time required to obtain a homogeneous mixture depends to a significant extent on the particle size of the starting material. Alternatively, we have recently shown that controlled coprecipitation results in a simpler method for achieving intimate mixing of Fe and Ce oxides [9]. The Fe–Ce interaction seems to occur through the formation of hematite-like and cubic ceria-like solid solutions. In the hematite-like solid solution, Ce cations are dissolved in the hematite structure, whereas Fe cations are dissolved in the cubic ceria structure. Such interactions were absent in samples prepared by physical mixing.

As far as catalytic applications are concerned, pure hematite (α-Fe_2O_3) or ceria (c-CeO_2) are not very active for N_2O decomposition [10]. For this reaction, the best catalyst is prepared

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by exchanging Fe^{III}/Fe^{II} salts (solid and gas) within a zeolite matrix, giving rise to high turnover rates even for low Fe loadings (ca. 0.5 wt% Fe) [11–15]. In this paper we show that Fe–Ce mixed oxides yield improved N_2O decomposition, much greater than those of the individual phases. Such a noticeable synergy is interpreted in terms of structural information derived from physicochemical analysis.

2. Experimental

2.1. Catalyst preparation

A series of coprecipitated iron-cerium oxide catalysts with 100, 95, 85, 50, and 0 at% Fe metal (Ce balance) was prepared by batchwise coprecipitation under vigorous stirring from 1 M aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka, p.a. 98–101%) and $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich 99.99%), with a 5.6 M NH_4OH solution. Both solutions were simultaneously added at a constant rate of 50 mL/h by a perfusion pump (Becton Dickinson SE 400) to a precipitating batch containing 500 mL of distilled water at the start. The addition of the precipitating agent (NH_4OH) was accomplished using a pH-stationary device (Radiometer Copenhagen; ABU91 Autoburette), maintaining the pH constant at 8.0 during precipitation. Temperature was kept at 343 K. The precipitate thus obtained was aged for 16 h with the mother liquor still under stirring at the reaction temperature, with pH maintained at 8.0. Then the precipitate was filtered out and washed with successive portions of 400 mL of distilled water at 323 K. The precipitates were dried in air at 333 K for 24 h. These solids are referred to as Fe100Ce0 (pure Fe), Fe95Ce5, Fe85Ce15, Fe50Ce50, and Fe0Ce100 (pure Ce).

2.2. Characterisation techniques

Powder X-ray diffraction (XRD) patterns were recorded in the 5–80° 2θ range in scan mode (0.02°, 2 s) using a Seifert 3000 XRD diffractometer equipped with a PW goniometer with Bragg–Brentano $\theta/2\theta$ geometry, an automatic slit, and a bent graphite monochromator. The unit cell parameters were obtained by refining the peak positions of the XRD patterns with a least squares refinement method using the CELREF program [16]. To determine peak positions, the peak profiles were fitted with the commercially available ANALYZE program (pseudo-Voigt function). Thermoanalytical measurements were carried out on Perkin-Elmer TGA7 and DTA-7 devices. The experiments were carried out with ca 50 mg of sample, under air flow, 60 $ml_N\,min^{-1}$, and a heating rate of 10 $K\,min^{-1}$ in the 303–1273 K range. Nitrogen adsorption isotherms were obtained at the temperature of liquid nitrogen (77 K), using a Micromeritics ASAP 2000 apparatus. Samples were degassed at 413 K for 12 h before the adsorption isotherm was determined. BET areas were computed from the adsorption isotherms ($0.05 < P/P_0 < 0.30$), taking a value of 0.164 nm^2 for the cross-section of the adsorbed N_2 molecule at 77 K.

Hydrogen temperature-programmed reduction (H_2-TPR) was carried out in a U-shaped quartz reactor connected to a QMS 200 Balzers Prisma quadrupole mass spectrometer for on-line gas analysis. The sample (50 mg) consisted of solid particles in the 250–300 µm range. The gas flow rate was 50 $ml_N\,min^{-1}$ (10% vol. H_2/Ar), and the heating rate was 10 $K\,min^{-1}$ (298–1073 K). The fragments $m/z = 2$ (H_2) and $m/z = 18$ (H_2O) were continuously monitored. Gas lines from the reactor to the inlet of the mass spectrometer were heated to 393 K to avoid water condensation. Quantification of the water signal was done through a calibration curve obtained with a high-purity CuO (99.9999%, Aldrich).

X-Ray photoelectron spectroscopy (XPS) was done with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Al-K_α ($h\nu = 1486.6$ eV) X-ray source. The samples were outgassed at room temperature within the pretreatment chamber of the spectrometer. Several pretreatments were performed to evaluate the effect of N_2O exposure. These involved heating up in helium at 823 K and N_2O exposure (4.5 mbar in He) at the same temperature. The binding energies of Ce 3d, Fe 2p, and C 1s core levels were determined, referencing to the binding energy of adventitious C 1s signal at a binding energy of 284.9 eV, which gives an accuracy of ±0.1 eV. Peak intensities were estimated by calculating the integral of each peak, after smoothing, subtracting an S-shaped (Shirley) background, and fitting the experimental curve to Lorentzian and Gaussian lines of variable proportion. Atomic ratios were then computed from the intensity ratios normalised by atomic sensitivity factors.

2.3. N_2O-decomposition activity tests

The activity measurements were carried out in a six-flow reactor [17] using 50 mg of precursor (particle size 250–300 µm). The following conditions were applied: 4.5 mbar N_2O (balanced with He), 3 bar-a total pressure, and temperature range of 473–873 K at GHSV = ~23,800 h^{-1}. Before the reaction, the precursor was activated both in He and air (flow of 50 $mL\,min^{-1}$) at 873 K (at a heating rate of 5 $K\,min^{-1}$) for 1 h. The reactor effluents were analysed by gas chromatography (Chrompack CP 9001) after 1 h reaction at each temperature. This time assured that the measurements were obtained under steady-state conditions for every temperature. Note that the space velocity used (GHSV = ~23,800 h^{-1}) was somewhat lower than that commonly used for Fe zeolites (>40,000 h^{-1}); low velocities were required to show substantial activity for this sort of catalyst in the range of 673–873 K.

3. Results and discussion

3.1. Activity results

The conversion of N_2O as a function of the reaction temperature is shown in Fig. 1. All of the catalysts showed substantial activity in the temperature range studied. The onset of the conversion occurred at around 623 K for the most active catalyst.

The mixed Fe–Ce catalysts were significantly more active than the pure Fe100Ce0 and Fe0Ce100 catalysts. The enhancement of activity at a certain temperature increased with increasing Ce content in the series. This effect can also be inter-