

Role of defect structure in structural sensitivity of the oxidation reactions catalyzed by dispersed transition metal oxides

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Abstract

For dispersed transition metal oxides, the specific catalytic activity in the reactions of CO and hydrocarbons oxidation was compared with the densities of bulk and surface defects that were estimated using a combination of diffraction and spectroscopic methods. On this basis, the oxide systems were classified with respect to the scale and origin of the structural sensitivity manifestation. The results were discussed from the point of view of the atomic structure of the most developed surface faces of these oxides and their stoichiometry ranges. The most active surface sites were found to be associated with the surface extended defects including those located at the outlets of bulk extended defects. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The structural sensitivity of catalytic reactions is one of the most important problems in heterogeneous catalysis [1,2]. It has been rather thoroughly studied for metals, while for oxides — especially for dispersed ones — the situation is far less clear due to the inherent complexity of studies of their bulk and surface atomic structure. For dispersed transition metal oxides, the manifestation of the structural sensitivity is

usually assigned either to the effect of particles morphology (different surface faces have a different atomic structure, and, hence, catalytic properties) or to defects changing in their vicinity the adsorption properties and reactivity of the surface centers. Since they are dependent upon the oxide nature and its genesis, such defects can be either of a pure surface type (vacancies, steps) or situated at the outlets of bulk extended defects (dislocations, stacking faults, twins). The most straightforward approach to estimation of the relative importance of these factors is to compare the specific catalytic activity with the density of bulk and/or surface defects. For the same chemically pure

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oxide phase, the linear dependence between the specific catalytic activity and the density of defects changed due to variation of the preparation procedure is the direct evidence that active centers are associated with those defects. Up to now, however, such quantitative data are hardly available. Earlier [3–16], by using a combination of diffraction and spectroscopic methods, the genesis of the bulk/surface defect structure of the oxides of copper, iron, cobalt, chromium, manganese was studied, and main types of defects were revealed, and their effect on the surface oxygen bonding strength and reactivity was elucidated. This work aims at elucidating the nature of the structural sensitivity of dispersed transition metal oxides in the reactions of carbon monoxide and hydrocarbons oxidation using the quantitative approach described above.

2. Experimental

As starting materials, nitrates, hydroxocarbonates, (oxo)hydroxides, oxalates, ammonium oxalatoferriate and ammonium dichromate of “pure for analysis” or “specially pure” grades were used. Oxides were usually prepared by the precursors’ thermal decomposition at 300–400°C with a subsequent annealing in air or in He flow in the range of temperatures up to 1100°C. Some details of the preparation procedures are given in Refs. [3–8].

2.1. TEM

Samples were examined in JEM-100 CX, JEM-200 C and JEM-400 C microscopes. Specimens were deposited onto a carbon film supported on a copper grid [3–5].

2.2. XRD patterns

XRD patterns were obtained with a URD-6 diffractometer (Germany) using the Cu K_β radiation. The Polycrystal program was used to

determine the structural parameters and estimate the densities of extended defects [6,8].

2.3. Relative densities of extended defects

The relative densities of extended defects were evaluated by the X-Ray Small Angle Scattering method (SAXS) using the Cu K_α radiation with a nickel filter and an amplitude analyzer [4,8].

2.4. IR spectra of the lattice modes

The IR spectra of the lattice modes of oxides were obtained using an M-80 spectrometer. For oxides with spinel and corundum-type structures, as the measure of the density of lattice extended defects changing the cations coordination in their vicinity, the relative intensity of the “defect” lattice bands absent for the “perfect” samples was used [8]. This procedure includes the decomposition of complex absorption contours into separate bands clearly developed in the spectrum and estimation of their relative integral intensity [13]. The ratio of the relative intensities of “defect” bands to those corresponding to Me–O vibrations in the regular polyhedra was shown to reasonably correlate with the density of extended defects, which were estimated by diffraction methods [16].

2.5. Surface chemical composition

The surface chemical composition was analyzed with XPS (an ESCALAB-3 spectrometer) and SIMS (an MS-7201 mass spectrometer) methods [8,12]. Only surface-pure samples (surface concentration of admixed cations less than 1%) were used here.

2.6. Surface-coordinatively unsaturated centers

Surface-coordinatively unsaturated centers were studied by the infrared spectroscopy of adsorbed test molecules (CO, NO) using an

IFS-113V B “Bruker” spectrometer. The isolated and clustered surface centers were differentiated using the low-temperature isotope dilution experiments in the adlayer of adsorbed test molecules [9,10,16]. As a measure of the surface sites concentration, the optical density of carbonyl (nitrosyl) bands corresponding to those sites and normalized to the surface area was used. This method is based upon the well-known proportionality between the optical density of the band corresponding to C–O (N–O) stretching in the test molecules and their surface coverage, the latter coincides with the number of adsorption centers at reasonably low adsorption temperatures. Usually, a complex absorption contour was decomposed into the individual components and their optical density was determined within a routine described in Ref. [12].

2.7. The heats of oxygen adsorption

The heats of oxygen adsorption and amounts of a weakly bound oxygen were determined using a high temperature Calvet microcalorimeter, TPD and electrochemical method [11,16]. Since a weakly bound oxygen was shown to be mainly located at defect centers for the majority of oxide systems studied here, its amount was used as a measure of the surface defect sites.

2.8. Catalytic properties

The catalytic properties in the reactions of carbon monoxide oxidation were studied using a

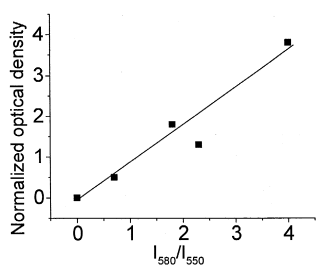


Fig. 1. Concentration of surface clustered defect centers characterized by the normalized optical density of carbonyl band [10] vs. the density of bulk extended defects characterized by intensity of the lattice modes “defect” absorption band [13] for α - Fe_2O_3 samples prepared from goethite.

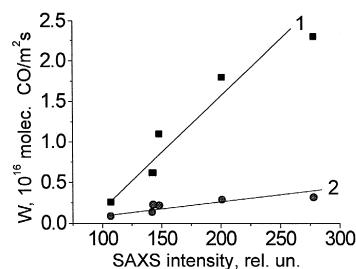


Fig. 2. The initial (1) and steady-state (2) rate of CO oxidation (1% CO + 1% O_2 in He, 140°C) vs. the density of bulk defects characterized by SAXS for α - Fe_2O_3 sample subjected to mechanical activation for different time [8].

microreactor with the vibrofluidized bed of catalysts. Catalytic activities were characterized by the reaction rate W (mol. CO/m² s) in differential conditions.

3. Results and discussion

The analysis of the experimental data obtained in this work allowed to classify the oxide systems according to the scale of structural sensitivity as follows.

3.1. Strongest manifestation of structural sensitivity

The strongest manifestation of the structural sensitivity (variation of the specific catalytic activity of the same oxide phase within 2–3 orders of magnitude) was revealed for oxides with a very narrow range of the surface and bulk nonstoichiometry (α - Fe_2O_3 , CuO). For such systems, the most developed surface planes are covered by tightly bound non-reactive bridging oxygen forms, while a weakly bound oxygen is located at the clustered defect centers [4,8,12,15]. For low- and middle-temperature samples (the temperature of calcination is less than 600–700°C [16]), the density of clustered surface defects correlates with the density of bulk extended defects, as shown in Fig. 1 for hematite samples. For high (up to 1100°C) cal-

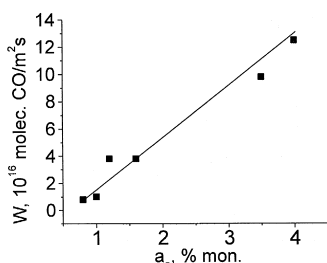


Fig. 3. The steady-state rate of CO oxidation (1% CO + 1% O₂ in He, 227°C) vs. the amount of weakly bound oxygen estimated by TPD method for α -Fe₂O₃ samples prepared from goethite.

ination temperatures, the bulk extended defects are annealed, and surface or near-surface defects (steps, patches of surface microphases of a different structure, dislocation networks) dominate [6,7]. For systems with high structural sensitivity, good linear dependencies of specific catalytic activity upon the density of bulk (Fig. 2) and/or surface extended defects (Fig. 3) were observed. As a rule, for these systems, the specific catalytic activity in the reactions of butane and butene combustion correlates with that in CO oxidation [16].

3.2. Moderate manifestation of structural sensitivity

A moderate manifestation of structural sensitivity (variation of the specific catalytic activity within 1–2 orders of magnitude) was revealed for oxide systems with a narrow range of the bulk nonstoichiometry, the surface layer stoichiometry broadly varying as dependent upon

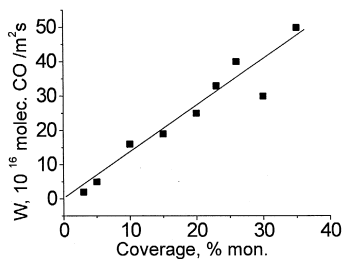


Fig. 4. The steady-state rate of CO oxidation (1% CO + 1% O₂ in He, 140°C) vs. the amount of weakly bound oxygen estimated by the electrochemical method [11] for Co₃O₄ samples prepared from various starting compounds.

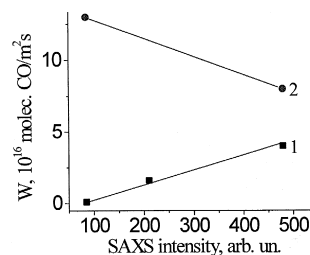


Fig. 5. The rate of CO oxidation vs. the density of bulk defects estimated by SAXS for Co₃O₄ samples prepared from carbonate and annealed at different temperatures. (1) Steady-state rate at 70°C, 1% of CO in air; (2) steady-state rate at 140°C, 1% CO + 1% O₂ in He.

the pretreatment and activity measurement conditions (Co₃O₄, CoO, NiO, stoichiometric Fe₃O₄, MnO₂, Mn₂O₃). For these systems, some regular centers located at weakly developed rough surface faces are able to coordinate on-top oxygen forms with moderate bonding strength and reactivity. Under reduction, such faces are usually rearranged forming clusters of coordinatively unsaturated reduced cations that are accompanied by the activity increase. Usually, for these oxides, the linear dependencies between the specific catalytic activity and the amount of weakly bound oxygen located at defect centers as well as on a part of the regular centers are observed (Fig. 4). However, due to the reconstruction of some faces under the reaction media effect, the dependencies of activity on the den-

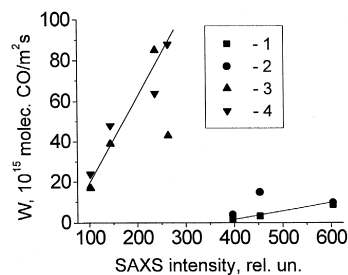


Fig. 6. The initial (1, 3) and steady-state (2, 4) rates of CO catalytic oxidation at 185°C (1% CO + 1% O₂ in He) vs. the integral density of bulk extended defects estimated by SAXS for α -Cr₂O₃ samples prepared from nitrate (1, 2) and ammonium bichromate (3, 4). The most developed surface faces are of the (0001) type for bichromate series and of (112–0) type for nitrate series.

sity of bulk or near-surface extended defects can vary as dependent upon the temperature of reaction and reaction mixture composition (Fig. 5). Besides — due to the difference in stoichiometry and reactivity of various faces of the same oxide — at the same density of bulk extended defects, the specific catalytic activity depends upon the particles morphology (Fig. 6).

3.3. Weak variation of specific catalytic activity

A weak (for 2–3 times) variation of specific catalytic activity was observed for spinel oxides with a broad range of bulk nonstoichiometry Mn_3O_{4+x} , Fe_3O_{4+x} . For such systems, a weak dependence of activity on genesis (defect structure) is explained by a big (up to a monolayer) amount of a moderately strongly bound and reactive oxygen located at regular surface sites, which is unequivocally determined by the sample stoichiometry governed by the reaction media effect.

4. Conclusions

For dispersed transition metal oxides, the strongest manifestation of structural sensitivity was revealed for oxides with a narrow range of bulk and surface stoichiometry. In this case, catalytic activity in the oxidation reactions is determined by defect centers able to coordinate weakly bound and reactive oxygen forms. The broader is the stoichiometry range, the weaker is the dependence of specific catalytic activity on the density of genetic defects.

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