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Defective Magnesium Oxides with Oxygen-Containing Anion Fragments Incorporated in the Oxide Structure

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Abstract—The synthesis of defective magnesium oxides from different precursors is reported. The formation of the defective oxides (which are catalytically active in free-radical reactions) as substitutional solid solutions is possible only via MgO hydration in a salt solution.

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Magnesium oxide is used as a catalyst and as a support for catalysts employed in one-electron transfer reactions. In particular, magnesium oxide catalyzes nonbranched-chain free-radical hydrocarbon pyrolysis. The activity of the oxide is due to its structure. MgO has a face-centered cubic lattice. Each magnesium cation is in the center of an octahedron and is surrounded by six O^{2-} ions. Likewise, each oxygen ion is surrounded by six magnesium cations. However, the oxidation state −2 is unstable for oxygen and the O^{2-} ion in a vacuum instantaneously loses an electron, releasing energy: $O + e = O^- - 1.4$ eV; $O^- + e = O^{2-} +$ 8.9 eV.

In the magnesium oxide crystal, the O^{2-} ion is stabilized by the Coulomb field of the surrounding magnesium ions. Therefore, if a cationic vacancy appears in the crystal, two nearest-neighbor oxygen ions will instantaneously lose one electron each. The resulting O^- species will diffuse as holes through the crystal bulk to the surface, where they will be stabilized. Chemically, O^- is a free radical, and it can be a catalytic site for radical reactions.

Various admixtures are used to increase the structural heterogeneity and catalytic activity of the oxide. They are introduced by impregnation or coprecipitation. Since MgO is thermodynamically very stable, the admixtures introduced in this way affect only its surface. The resulting active sites are annealed away rapidly at high reaction temperatures. In order to produce charge heterogeneity and enhance the thermal and reactive stabilities of magnesium oxide, admixtures should be introduced directly into the structural units. This is possible only during oxide–hydroxide–oxide restructuring. We suggest the following original synthesis method: commercial magnesium oxide is calcined at 1073 K and is then hydrated in a concentrated magnesium acetate solution until complete conversion into magnesium hydroxide, and the hydroxide is dried and calcined at high temperatures. It was demonstrated that hydroxoacetates of variable composition form already at the hydration stage. This reduces the hydroxide–oxide conversion temperature from 410 to 370°C. Above the temperature at which the acetates decompose to carbonates, the magnesium oxide structure contains incorporated distorted carbonate groups. The oxygen atoms of the carbonate groups are shared with the oxygen framework of the oxide [1]. Similar data were obtained for MgO hydration in a magnesium nitrate solution. The MgO samples thus prepared do not lose their defectivity upon calcination at 1273 K and retain their high activity in the free-radical pyrolysis of hydrocarbons after 90-h-long operation.

Here, we report the synthetic conditions for defective magnesium oxides. In particular, we address the issues of whether the hydration stage is necessary and is not it impossible to obtain the same product directly by magnesium salt calcination.

EXPERIMENTAL

We compared the structural features of magnesium oxide samples obtained from different precursors, namely, commercial magnesium carbonate, commercial magnesium carbonate hydroxide $Mg(OH)_2 \cdot MgCO_3 \cdot 2H_2O$, and defective $MgO/MgAc_2$ synthesized by the hydration of commercial magnesium oxide in a magnesium acetate solution followed by drying to obtain magnesium hydroxide and calcination yielding defective magnesium oxide. $MgO/MgAc_2$ was calcined at 350 K until the acetate traces were converted into carbonate. Next, the precursors were calcined at 673 K for 6 h, the temperature at which magnesium carbonate decomposes to magnesium oxide. After that, all samples were calcined at 1073 K for 6 h.

Dried and calcined samples were examined by thermogravimetric analysis, IR spectroscopy, diffuse

X-ray diffraction data for magnesium oxide samples

Sample no.	Precursor	a, Å	β_2/β_1	D_{111}, Å	$\Delta d/d$	$\rho \times 10^{-6}$, g/cm^3
		±0.0002*				
1	$MgCO_3$	4.2112	1.200	1500	–	0
2	$Mg_2CO_3(OH)_2$	4.2136	1.372	600	0.0003	0.63
3	$MgO/MgAc_2$	4.2183	1.878	1200	0.0017	1.78
4	MgO	4.211	–	–	–	–

*Accuracy of unit cell parameter measurements.

reflectance spectroscopy, and electron microscopy [1, 2]. X-ray diffraction patterns were obtained on a D-8 diffractometer (Bruker) using Cu$K\alpha$ radiation. A graphite monochromator was placed in the reflected beam to eliminate $K\beta$ radiation and to reduce the background. The $K\alpha1$–$K\alpha2$ doublet was resolved by using Bruker's standard software. Unit cell parameters were determined by least squares refinement. The mean effective coherent-scattering domain (CSD) and microdistortion sizes were determined using two orders of reflections in the [111] direction. To separate the physical broadening out of the line profile, we used an annealed silicon powder as the standard. Diffraction peak profiles were fitted to a pseudo-Voigt function (superposition of Cauchyan and Gaussian functions). Since the diffraction intensity profile is dominated by the Cauchyan contribution, the physical broadening can be determined with sufficient accuracy by subtracting the line of the standard from the observed peak profile and the D and $\Delta d/d$ values can be separated using the $\beta\cos\theta = f(\sin\theta)$ plot:

$$\beta_i\cos\theta_i = \lambda/D + 4\Delta d/d\sin\theta_i,$$

where β_i is the physical broadening of the diffraction line, λ is the radiation wavelength (λCu = 1/54178 Å), θ_i is the diffraction angle, D is the mean effective particle size (CSD), and $\Delta d/d$ is the microdistortion of the crystal lattice. The data thus obtained are listed in the table.

IR spectra were recorded on a Bomem MB-102 Fourier spectrometer using the CsI pellet technique.

RESULTS AND DISCUSSION

All reflections observed in the X-ray patterns of the samples are from the MgO phase. For the defective oxide $MgO/MgAc_2$, the line near the (422) reflection after the separation of the $K\alpha1$ line is broadened and shifted relative to the same line for the other samples. The refined unit cell parameters are presented in the table.

An analysis of the line half-widths due to physical broadening demonstrated that the β_{222}/β_{111} ratio varies from one sample to another, remaining within the limits of $\cos\theta_1/\cos\theta_2 < \beta_{222}/\beta_{111} < \tan\theta_2/\tan\theta_1$. The numerical values of β_{222}/β_{111} indicate that the lines of sample 1 are broadened only owing to the small particle size, while the lines of samples 2 and 3 are broadened owing to both the small particle size and microdistortions. The contribution from the microdistortions to the line broadening is greater for sample 3 than it is for sample 2 since the β_{222}/β_{111} ratio for sample 3 is closer to $\tan\theta_2/\tan\theta_1$ than the same ratio for sample 2. The line broadening analysis demonstrated that, for sample 1, the CSD size ~1500 Å and there are no lattice microdistortions. For sample 2, the CSD size is 2.5 times smaller (~600 Å) and there are slight lattice microdistortions ($\Delta d/d = 0.0003$).

The real structural characteristics of sample 3 are different: the CSD size is ~1200 Å, and the microdistortions are 6 times larger than those in sample 2. Calculation of the density of dislocations randomly distributed in the particle bulk (ρ) using the formula $\rho = \dfrac{2\sqrt{3}\Delta d/d}{Dhklb}$ demonstrated that ρ for sample 3 is ~3 times larger then ρ for sample 2 and that sample 1 has no dislocations at all.

These data confirm that the sample prepared by MgO hydration of in a magnesium acetate solution is more defective than magnesium oxide obtained by conventional methods. It is due its higher defectivity that sample 3 is catalytically more active.

The IR absorption band of $MgO/MgAc_2$ is much broader and more asymmetric than the standard MgO band [2]. The presence of distorted carbonates in the structure of defective magnesium oxide is indicated by absorption in the 1400–1500 cm^{-1} range, which is characteristic of the CO_3^{2-} ion. The absorption intensity due to this ion for samples 1, 2, and 4 is negligible and is attributable to surface carbon dioxide. The oxygen atoms of built-in carbonates belong to the oxygen framework of the oxide, and the carbon atom occupies the site of a magnesium cation, introducing a positive charge higher than +2. The weakening of the fundamental absorption band of MgO and the change in the shape its contour are evidence that the structure of $MgO/MgAc_2$ is highly defective. Another significant fact is that the absorption maximum of MgO in this material is shifted to lower frequencies by 56 cm^{-1}. Since the MgO microcrystallites have a high, cubic

symmetry, any change in the fundamental absorption band is indicative of local changes in the closest environment of MgO. For example, the formation of lattice vacancies alters the vibration conditions for the particles in the immediate vicinity of these vacancies: the existence of an "empty" space is favorable for an increase in the vibration amplitude and, accordingly, a decrease in the vibration frequency of the particles nearest to the vacancy. In our case, the observed marked decrease in Mg–O vibration frequency possibly indicates that the magnesium oxide lattice contains not only foreign ions, but also cationic vacancies induced by these ions. As was mentioned above, the cationic vacancies favor the formation of O^- active sites. The foreign cations having a charge above +2 are also favorable for the formation of radical active sites.

Thus, the synthesis of defective magnesium oxides can be carried out only via the hydration of commercial magnesium oxide in a salt solution. It was found that the oxygen-containing anions of the salt incorporate in the anionic framework of the hydroxide/oxide. The residue of the anion whose oxygen atoms belong to the oxygen framework of the oxide incorporates into the oxide structure by occupying the site of a virtual magnesium cation. Some of cationic vacancies remain empty, and the others are occupied by transformed anion residues with a positive charge other than +2.

This restructuring takes place in the temperature range of defective magnesium oxide formation. At $T \geq 700°C$, the defective oxide is completely formed and appears as a substitutional solid solution. This structurally homogeneous phase persists after calcination at 1000°C for 6 h. The defective magnesium oxides are catalytically active in the free-radical pyrolysis of hydrocarbons.

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