Mechanochemical Reactions of Hydrated Oxides

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Thermodynamic calculations have shown that chemical reactions in mixtures of hydrated oxides are more advantageous than those in anhydrous oxide mixtures. Mechanochemical reactions of calcium oxide with hydrated and anhydrous aluminum, silicon, titanium, vanadium, and tungsten oxides are investigated experimentally. It was shown that the reaction rate is correlated with the thermodynamic reaction potentials, and also with differences in the proton affinity of the oxides. The influence of water additives on the synthesis rate was investigated. It was found that the reaction rate goes through a maximum in its dependence on water content. © 1994 Academic Press, Inc.

INTRODUCTION

Solid state mechanochemical synthesis is a promising method in chemistry (1). Substances containing constitutional water may be thought as undergoing solid state reactions. However, constitutional water contained in solids is released in the course of the mechanochemical activation, and synthesis may occur in the presence of liquid phases due to release of water.

The question as to how water influences solid state mechanochemical reactions is not new. One must consider two fundamental experimental facts:

(1) the presence of small amounts of water adsorbed at the surface of powders results in reactions analogous to those in concentrated solutions (2);

(2) no relationship exists between reaction rate during mechanical treatment and the solubility of reactants (3). In some recent work data were reported on both the inhibiting and the promoting effects of water on mechanochemical reactions. The latter is most pronounced in acid–base reactions between oxides. Moreover, this effect manifests itself both for free and for constitutional water.

Pajakoff (4) studied a series of mechanochemical reactions of hydrated compounds, mainly oxalates. He encountered formation of a "honey-like" mass during the reactions, from which the reaction products—solid complex crystallohydrates—finally crystallized. The authors (5) obtained a high-performance lithium ferrite by mechanochemical reaction between LiOH and α-FeO(OH). Liao and Senna (6) investigated the reaction between $Mg(OH)_2$ and SiO_2 and established the active role of proton transfer.

It can be assumed that the promotion of reactions in such mixtures is produced by (a) formation of liquid phases or (b) water elimination in the course of the hydrate decomposition. The first occurs in low-melting eutectics of mixtures of hydrates and the second is accompanied by water evolution due to mechanical treatment (7). As has already been stated (8), dehydration and synthesis may proceed simultaneously under conditions where hydrated oxides decompose without melting.

In this paper we discuss findings concerning the interaction of calcium oxide (base oxide) with hydrated oxides of aluminum, silicon, titanium, vanadium, and tungsten (acid oxides). We attempted to elucidate the effect of water on the reactions between oxides, which involve an acid–base mechanism.

EXPERIMENTAL

Reagents. CaO was prepared from pure grade calcium carbonate calcined at 1373 K for 4 hr. Hydrated silicon oxide was in the form of silicon acid, with a water content of 0.63 mole per mole SiO_2. Hydrated aluminum oxide was used as a chemically pure reactant—hydrargillite, $Al(OH)_3$.

The other hydrated oxides were chemically pure solids H_2TiO_3, H_2WO_4, $H_2V_2O_6$.

Apparatus. Mechanochemical reactions were performed in an AGO-2 planetary mill (9) with balls and thimbles made of titanium (thimble volumes 150 cm³, ball diameters 8 mm, ball masses 200 g, mass of mixture 10g). The thimble rotation frequency was 720 rpm, which corresponds to centrifugal acceleration of 400 m/sec². Intensive cooling of thimbles by water flow was realized in the planetary mill, and the average temperature never exceeded 343 K on the wall of the thimble.

Procedure. Mixtures were activated mechanically for a few minutes in the planetary mill. The activated mixtures were investigated by different methods. The conversion

Reaction	$\Delta G^{\circ}_{298, \text{reac.}},$ kJ/mol
1. $CaO + \alpha\text{-}Al_2O_3 = CaAl_2O_4$	-23.0
$CaO + Al_2O_3 \cdot H_2O = CaAl_2O_4 + H_2O$	-30.5
2. $CaO + Al_2O_3 + 2SiO_2 = CaAl_2Si_2O_8$	-76.3
$CaO + Al_2O_3 \cdot H_2O + 2H_2SiO_3 = CaAl_2Si_2O_8 + 3H_2O$	-114.1
3. $CaO + SiO_2 = CaSiO_3$	-89.4
$CaO + H_2SiO_3 = CaSiO_3 + H_2O$	-173.5
$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O$	-33.0
$Ca(OH)_2 + H_2SiO_3 = CaSiO_3 + 2H_2O$	-117.2
4. $CaO + TiO_2 = CaTiO_3$	-89.8
$CaO + H_2TiO_3 = CaTiO_3 + H_2O$	-164.2
$Ca(OH)_2 + TiO_2 = CaTiO_3 + H_2O$	-33.9
$Ca(OH)_2 + H_2TiO_3 = CaTiO_3 + 2H_2O$	-108.2
5. $CaO + SiO_2 + TiO_2 = CaTiSiO_5$	-118.3
$CaO + H_2SiO_3 + H_2TiO_3 = CaTiSiO_5 + 2H_2O$	-213.2
6. $CaO + V_2O_5 = CaV_2O_6$	-145.2
$CaO + H_2V_2O_6 = CaV_2O_6 + H_2O$	-138.3
7. $CaO + WO_3 = CaWO_4$	-166.0
$CaO + H_2WO_4 = CaWO_4 + H_2O$	-236.1

fraction was quantitatively estimated by chemical analysis
of the activated mixtures through the free calcium oxide
content, using the ethyl-glycerate method [10]. X-ray dif-
fraction patterns were obtained on a DRON-3 diffrac-
tometer (Cu$K\alpha$ radiation). Infrared spectra were recorded
on a Specord-75IR spectrometer.

RESULTS AND DISCUSSION

The thermodynamic calculation of isobaric–isothermic
potentials for reactions of anhydrous and hydrated oxides
are presented in Table 1. As a rule, reactions of hydrated

acidic oxides are thermodynamically the most advanta-
geous. Only in the case of calcium vanadate synthesis are
the potentials for reactions of anhydrous and hydrated
vanadium oxides approximately equal. The reactions of
$Ca(OH)_2$ with the acid oxides are less advantageous than
those of CaO, because formation of calcium hydroxide is
an exothermic process.

The data for mechanochemical reaction of calcium ox-
ide with anhydrous and hydrated oxides are presented in
Fig. 1, where α is the conversion fraction equal to the
proportion of calcium bound in the product compound
($\alpha = Ca_{\text{bound}}/Ca_{\text{total}}$), and t is the time of the mechanical
treatment. It can be seen that anhydrous silicon and tita-
nium oxides react very slowly both with calcium hydrox-
ide and oxide. The reaction rates of CaO and $Ca(OH)_2$ with
hydrated oxides are comparatively high. The reaction rate
with $Ca(OH)_2$ is highest, although it is less advantageous
thermodynamically. As a whole, for the entire series of
reactions under study, a correlation exists between reac-
tion potentials and reaction rates. This is to be seen from
Fig. 2, where the data for mechanochemical reaction of
anhydrous and hydrated oxides are presented, and from
Fig. 3, where the correlation between the thermodynamic
and kinetic data is shown. In Fig. 3 the reaction rate V
was determined from the conversion fraction for a speci-
fied time ($V = \alpha/t$).

There are some departures from these correlations. As
mentioned above, the reaction rate for calcium hydroxide
is higher than that for CaO. This fact may be explained
by formation of intermediate amorphous states. In the
synthesis of calcium titanate and silicate the thermody-
namic potentials are equal but the rates are different. This
fact may be explained by the structural correlation of the
starting material and final product. Calcium titanate has
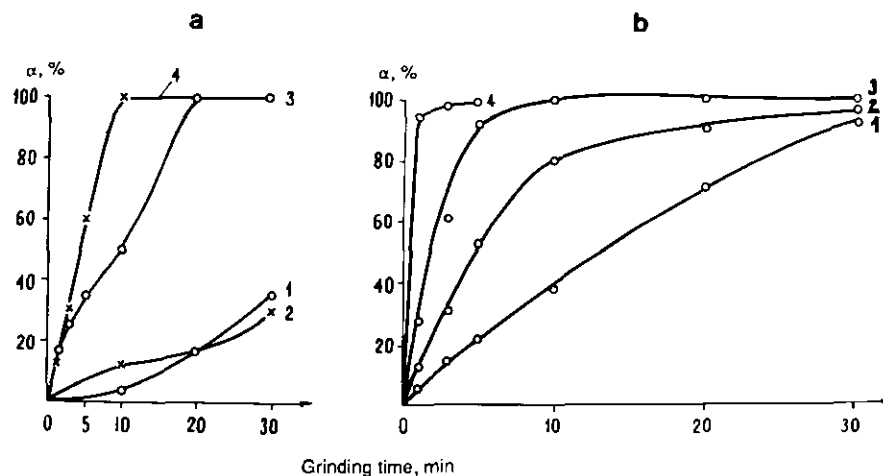the perovskite structure, in which vacant sites between

FIG. 1. The conversion fraction (α) as a function of grinding time: (a) 1—$CaO + SiO_2$, 2—$Ca(OH)_2 + SiO_2$, 3—$CaO + H_2SiO_3$, 4—$Ca(OH)_2 + H_2SiO_3$, (b) 1—$CaO + TiO_2$ (rutile), 2—$CaO + TiO_2$ (anatase), 3—$CaO + H_2TiO_3$, 4—$Ca(OH)_2 + H_2TiO_3$.
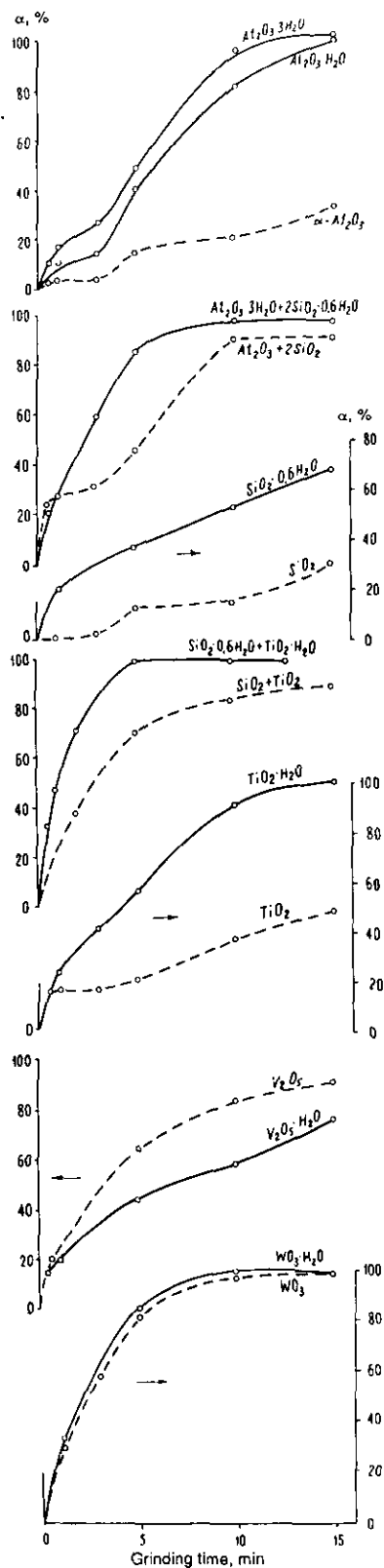
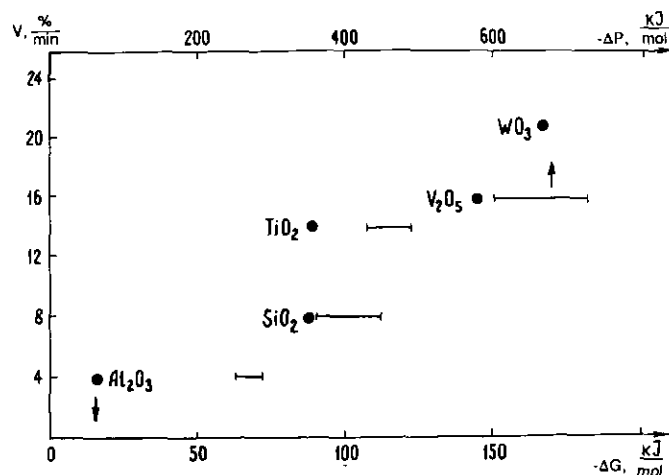FIG. 2. The dynamics of the mechanochemical interaction of calcium oxide with anhydrous and hydrated oxides.

FIG. 3. The correlation between thermodynamic potentials (ΔG), proton affinity (ΔP), and mechanochemical reaction rate.

TiO_6 octahedra exist. Calcium ions occupy these sites with a minimal energy expenditure. In contrast, no significant difference is observed between the rates of interaction of $Al_2O_3 \cdot 3H_2O$ (hydrargillite) and $Al_2O_3 \cdot H_2O$ (boehmite) with calcium oxide. This fact may be explained by transformation of hydrargillite into boehmite by mechanical activation (1).

Corresponding results are presented in Fig. 4 for reactions of mixtures of calcium and titanium oxides as a function of water content. In one experiment a hydrated titanium oxide was annealed at various temperatures (688–1073°C) to obtain oxides with variable water contents (curve 1). In another experiment "free" water was doped into mixtures of anhydrous oxides before treatment (curve 2). In the first case the conversion fraction increased with water content. In the second case the plot
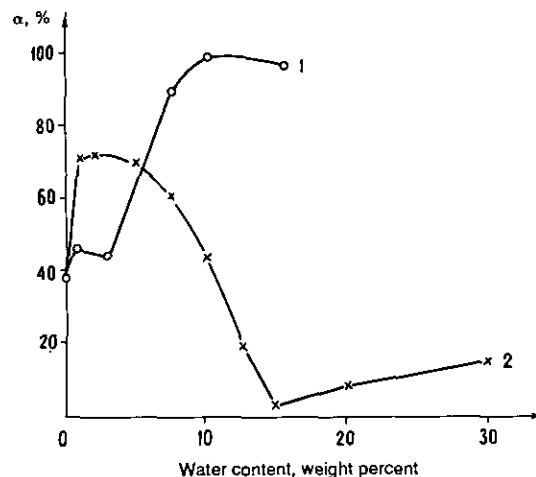

FIG. 4. The influence of water content on the interaction of calcium oxide with titanium oxide: (1) bonded water; (2) "free" water.
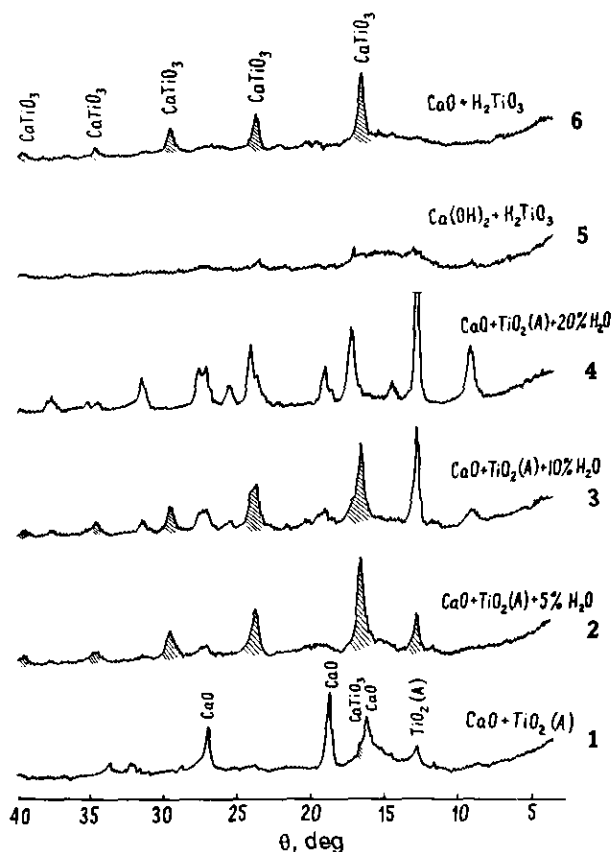
FIG. 5. The X-ray diffraction patterns of the activated mixtures CaO + TiO₂ (anatase) for varied levels of water content (1–4) and for the mixtures Ca(OH)₂ + H₂TiO₃ (5) and CaO + H₂TiO₃ (6).

active role in the formation and crystallization of the final product.

Similar data were obtained for the reaction of calcium oxide with silicon oxide. In Fig. 6 infrared spectroscopy data are presented for individual components, and for their mixtures after mechanical activation. There are essentially no changes in the initial components (spectra 1 and 2). The activated mixtures absorb infrared radiation in the region from 1005 to 925 cm⁻¹; these peaks may be associated with formation of calcium silicate (spectra 3 and 4).

The quantitative characteristics for acid–base properties of oxides reside in their affinity to protons (12). To determine the affinity to protons a method has been developed consisting in the adsorption of test molecules onto the oxide surface and in the analysis of variations of the vibration frequency of surface OH⁻ groups (13). This method has been used earlier to test the affinity to protons for a large number of oxides (13). The difference in affinity to protons for the reacting oxides may be a quantitative characterization of acid–base reactions. In Fig. 3 the difference in affinity to protons ($\Delta P = P_{CaO} - P_{Me_xO_y}$) is drawn against the reaction rate. It can be seen that the reaction rate rises both with the increasing difference in affinity to protons and with increasing thermodynamic potentials of reactions.

Thus, it is necessary to select the oxides with maximal differences in acid–base properties in order to realize
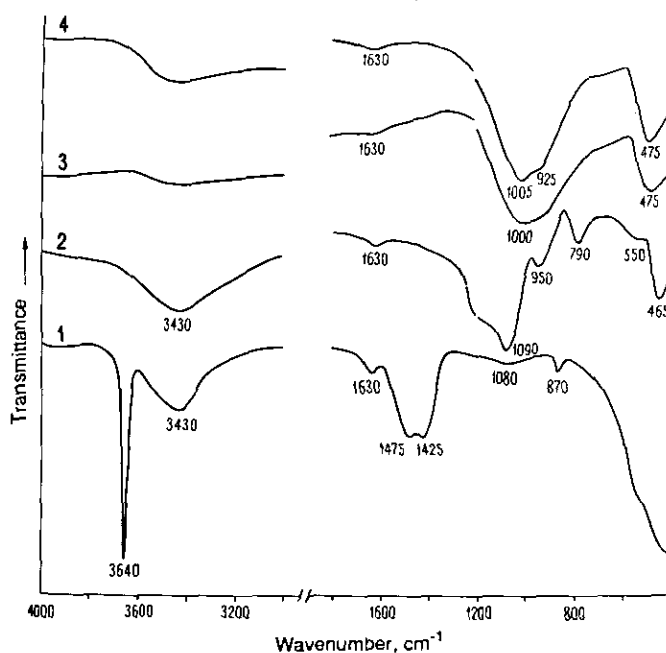
of the conversion fraction vs water content has extrema: a maximum at the initial stage (1–3% H₂O) and a minimum at about 15% H₂O. Finally, the reaction rate increases again with water content. The X-ray data in Fig. 5 indicate the course of curve 2 in Fig. 4. The reaction products are absent at a water content of 20%. The reason for the decrease of the conversion fraction with the increase of water content may be in the setting of the mixture as a cement—a feature that was experimentally observed on some occasions. This effect was not observed for curve 1 in Fig. 4.

The highest reaction rate was found for the reaction of calcium hydroxide with hydrated titanium oxide. No crystalline phases were detected in the X-ray diffraction patterns (Fig. 5, curve 5). An X-ray amorphous product formed in which calcium oxide was bonded chemically. In our opinion a "solid" solution of hydrates forms via hydrogen bonding; it is known that water molecules are dissociated in hydrated titanium oxide (11). Moreover, the reaction rate for calcium oxide is slower, but a crystalline product forms. These data testify that protons play an

FIG. 6. The infrared spectra of initial activated reactants Ca(OH)₂ (1) and SiO₂·0.63H₂O (2), and of products of mechanochemical interactions Ca(OH)₂ + SiO₂·0.63H₂O (3) and CaO + SiO₂·0.63H₂O (4).

the most effective synthesis of complex oxides or dope additives into oxides so as to intensify their acid–base properties.

The above mentioned principles have been applied to the synthesis of anortite (calcium–aluminum silicate) and sphene (calcium–titanium silicate), carried out by mechanical activation of hydrated oxides (Table 1, Fig. 2). It is known from catalysis practice that mixtures of aluminium and silicon oxides exhibit the strongest acid properties. Indeed, the reaction rate is considerably higher than for binary mixtures (Fig. 2). By contrast, the reaction rates for mixtures of titanium and silicon oxides with calcium oxide do not exceed those for calcium oxide and titanium oxide.

Such a mechanochemical synthesis is very appropriate because it combines mechanical activation with chemical acid–base interactions. It is hoped that the present work will promote use of this method in applied chemistry.

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