Cordierite-Like Catalyst Supports Based on Clay Materials

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Abstract—The possibility of lowering the temperatures of crystallization of spinel-like cordierite, mullite, $MgAl_2O_4$, and corundum was studied. The following naturally occurring clay materials were used for the synthesis of supports: bentonite, clay, and kieselguhr. The effect of the preparation procedure on the structure and texture characteristics of the resulting supports was found. The composition of the resulting samples varied over the following ranges: clay material, from 45 to 60%; Al_2O_3, from 30 to 42%; and MgO, from 10 to 20%. Conditions responsible for spinel formation in cordierite and mullite phases over the temperature range 1050–1150°C were found. At the same parent composition, the thermal stability of supports prepared by coprecipitation was higher than that of composites prepared by mechanical mixing, as found using X-ray diffraction analysis and measuring specific surface areas and mechanical strength. The supports synthesized are promising for the preparation of supported catalysts for high-temperature processes.

INTRODUCTION

Protecting the environment against industrial pollution (including automobile-exhaust emission control) represents one of the most important social problems.

Oxidation in the presence of supported catalysts is the simplest and most efficient method of air purification. Very stringent requirements (mechanical strength and thermal stability [1, 2]) are imposed on these catalysts.

To develop exhaust emission-control catalysts that are highly efficient, stable, and resistant to catalyst poisons, supports with versatile properties are required. These supports are responsible for the complete oxidation of all of the gaseous environmental pollutants [3, 4].

A spinel-type or spinel-like-type structure is most appropriate to these supports. This structure is prepared by the introduction of mineralizers into the bulk of Al_2O_3 [5–7]. A cordierite support, which exhibits high mechanical strength, hardness, good thermal conductivity, and a low thermal-expansion coefficient, belongs to these materials [8, 9].

Cordierite is usually prepared by mixing clay materials, talc, and compounds based on Al_2O_3 followed by treatment at ~1300°C. The sintering temperature can be decreased by the better homogenization of components, for example, by coprecipitation.

The aim of this work was to synthesize cordierite-like and mullite-like phases by the precipitation of aluminum hydroxide in clay materials (clay, bentonite, and kieselguhr) and MgO.

EXPERIMENTAL

Four support samples were prepared by the precipitation of an aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ in an aqueous suspension of clay, kieselguhr, or bentonite and MgO. A 2 M Na_2CO_3 solution was used as a precipitating reagent. The precipitation was performed using a semibatch method at a constant pH value; next, the precipitate was treated by a standard procedure including aging, filtration, washing until the absence of NO_3^- and Na^+ ions from the precipitate, and drying. Two samples were prepared by the mechanical mixing of components; the composition of these samples was analogous to the composition of precipitated samples. Pure aluminum hydroxide was prepared by precipitation; thereafter, dry components were thoroughly mixed. The compositions of the resulting samples are given below.

Samples D1–D4 (precipitated)

    D1: 48% clay, 42% Al_2O_3, and 10% MgO.

    D2: 60% kieselguhr, 30% Al_2O_3, and 10% MgO.

    D3: 45% clay, 35% Al_2O_3, and 20% MgO.

    D4: 50% bentonite, 37% Al_2O_3, and 13% MgO.

Samples D5 and D6 (mechanical mixtures)

    D5: 50% clay, 35% Al_2O_3, and 13% MgO.

    D6: 50% bentonite, 37% Al_2O_3, and 13% MgO.

Calcination was the main stage of support formation. Complicated physicochemical processes, polymorphic transformations, and chemical reactions occurred in the course of this stage. The main characteristics of the resulting samples are phase composition, mechanical strength, overall shrinkage upon calcination at 1150°C, specific surface area, total porosity, and moisture capacity. These characteristics were deter-

Table 1. Physicomechanical characteristics of supports calcined at 1150°C

Sample	Compacting pressure, kg/cm^2	Mechanical strength, kg/cm^2	Linear shrinkage, %	Apparent density, g/cm^2	Porosity, %	Specific surface area, m^2/g	Moisture capacity, %
D1-1	1000	150	4	1.2	54	10	41
D1-2	2000	230	2	1.6	40	9	26
D2-1	1000	125	4	1.3	70	6	44
D2-2	2000	180	2	1.8	68	6	34
D3-1	1000	390	5	1.5	60	8	30
D3-2	2000	490	2	1.8	46	8	28
D4-1	1000	300	4	–	–	–	–
D4-2	2000	335	1	2.1	35	8	25
D5-2	2000	275	1	2.2	57	11	25
D6-1	1000	200	1	–	–	–	–
D6-2	2000	355	1	2.0	42	11	25

Table 2. Mechanical strength and linear shrinkage of samples D1–D4 sequentially calcined at 600 and 1150°C

Parameter	D1-1	D1-2	D2-2	D3-2	D4-2
Mechanical strength, kg/cm^2	290	370	300	510	455
Linear shrinkage, %	4	1	1	1	2

mined after the pelletization of supports at 1000 and 2000 kg/cm^2 with the use of graphite as a lubricating additive (samples D1 and D2 were pelletized at 1000 and 2000 kg/cm^2, respectively). The mechanical strength of samples was determined by an axial fracture test using a hydraulic press. The specific surface area was determined by the BET method, and the total porosity was found by the impregnation of samples with benzene. The moisture capacity was determined on boiling in an aqueous medium. The X-ray diffraction analysis was performed on a TUR-62 diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the physicochemical characteristics of palletized supports after calcination at 1150°C. According to the experimental data, an increase in the pressure of pelletization increased the mechanical strength of samples and only slightly affected the linear shrinkage. An increase in the concentration of MgO also increased the mechanical strength. Sample D3 containing 20% MgO, which was prepared by precipitation, exhibited the highest mechanical strength. Moreover, precipitated samples containing clay or bentonite were stronger than supports based on kieselguhr. This is likely due to the plasticizing properties of clay and bentonite. A higher dispersity of parent clay components can facilitate the sintering of composites. To inhibit sintering, some samples were heated at 600°C, palletized, and calcined once again at 1150°C. As a result of this, the formation of materials was improved, and the mechanical strength of the resulting support was increased (Table 2).

The results of measurements of the specific surface areas of the resulting supports after drying at 100°C (D1, 110 m^2/g; D2, 70 m^2/g; D3, 92 m^2/g; and D4, 133 m^2/g) are indicative of the high dispersity of the parent mineralizers and, correspondingly, of the effect of bentonite on the surface area of the support at equal concentrations of components. The clay material affects the characteristics of samples. For example, the initial surface area of sample D1 containing the greatest amount of Al$_2$O$_3$ was lower than that of a bentonite-containing sample. The mechanical strengths of precipitated samples and composites prepared by the mechanical mixing of components based on bentonite and clay differed only slightly. The use of kieselguhr results in a decrease in the mechanical strength. This is likely due to the better plasticizing properties of bentonite and clay, as compared with kieselguhr.

In addition to mechanical strength, the supports should exhibit appropriate structure and texture. The introduction of clay mineralizers into precipitated aluminum hydroxide significantly affects the formation of the macroporosity of composites. After calcination at 1150°C, a kieselguhr-containing support (D2) exhibited the highest total porosity. Samples D5 and D6 (mechanical mixtures) agglomerated more slowly because of insufficient homogeneity with the retention of a specific surface area equal to 11 m^2/g.

Thus, texture parameters are responsible for the mechanical characteristics of supports (see Tables 1 and 2). The porosity of the majority of samples listed in Table 1 was sufficiently high; this allowed us to impregnate them with solutions containing active components. The moisture capacity, which was higher in precipi-

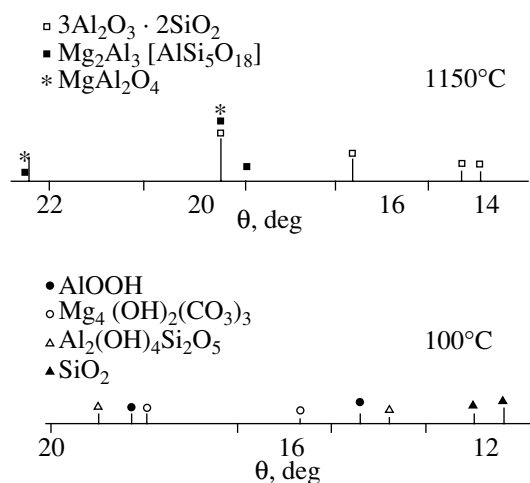**Table 3.** Phase composition of supports calcined at 1150°C

Sample	Composition	Preparation method	Phase composition	Dispersity, Å
D1	48% clay, 42% Al_2O_3, 10% MgO	Precipitation	Mullite $3Al_2O_3 \cdot 2SiO_2$; α-Al_2O_3; cordierite $Mg_2Al_3[AlSi_5O_{18}]$	Mullite $3Al_2O_3 \cdot 2SiO_{2(210)}$ 135
D2	60% kieselguhr, 30% Al_2O_3, 10% MgO	Precipitation	α-Al_2O_3; $MgAl_2O_4$, weak reflections; mullite $3Al_2O_3 \cdot 2SiO_2$ weak reflections; MgO, traces	α-$Al_2O_{3(104)}$ 210
D3	45% clay, 35% Al_2O_3, 20% MgO	Precipitation	Cordierite $Mg_2Al_3[AlSi_5O_{18}]$; mullite $3Al_2O_3 \cdot 2SiO_2$; α-Al_2O_3	Cordierite $Mg_2Al_3[AlSi_5O_{18}]_{(311)}$ 190
D4	50% bentonite, 37% Al_2O_3, 13% MgO	Precipitation	Cordierite $Mg_2Al_3[AlSi_5O_{18}]$; mullite $3Al_2O_3 \cdot 2SiO_2$; $MgAl_2O_4$, traces	Cordierite $Mg_2Al_3[AlSi_5O_{18}]_{(311)}$ 150
D5	50% bentonite, 37% Al_2O_3, 13% MgO	Mechanical mixing	Mullite $3Al_2O_3 \cdot 2SiO_2$, crystalline; α-Al_2O_3, traces	Mullite $3Al_2O_3 \cdot 2SiO_{2(210)}$ 190
D6	50% clay, 37% Al_2O_3, 13% MgO	Mechanical mixing	Mullite $3Al_2O_3 \cdot 2SiO_2$; $MgAl_2O_4$, weak reflections; α-Al_2O_3, traces	Mullite $3Al_2O_3 \cdot 2SiO_{2(210)}$ 170

tated samples, was indicative of the possibility of impregnating. Moreover, the precipitated samples exhibited higher specific surface areas, and spinel formation and sintering processes occurred at lower calcination temperatures than in the case of mechanical mixtures. As the temperature was increased in the course of spinel formation, sintering and the formation of a framework structure came into play. In this case, the density and mechanical strength increased and the specific surface area decreased. Pseudoboehmite prepared by precipitation exhibited a high specific surface area; in this case, the dispersity of the precursor ($AlOOH_{(140)}$) was 20–40 Å. The support based on boehmite–bentonite exhibited the highest specific surface area of 133 m²/g (sample D4). After calcination at $T = 600°C$, when a transition to γ-Al_2O_3 occurs, the specific surface area of this sample increased to 207 m²/g. After sintering at $T = 1150°C$, the specific surface area dramatically decreased to 8 m²/g. The montmorillonite structure of bentonite, which is characterized by a weak bond between layers, a strong swelling in an aqueous medium, and a high dispersity, is responsible for agglomeration in the course of calcination. However, these changes have no effect on the supporting of an active phase.

In addition to the preparation procedure, the nature of the components used affects the formation of spinel phases. Table 3 summarizes the phase composition of the samples.

Structure formation primarily depends on initial phase formation, which, in turn, depends on synthesis conditions. The homogeneity of a medium in the course of synthesis is of particular importance. Precipitation conditions play an important role in the formation of the properties of a given catalyst mass because of changes in the dispersity and chemical and phase composition of the resulting precipitates. It was found that, in the precipitation of aluminum hydroxide and aluminosilicate systems, the introduction of another component increased the specific surface area [10]. This was observed in the test system when $Al(OH)_3$ was precipitated in a medium of a clay material and MgO. The properties of catalyst masses prepared based on clay materials strongly depend on the initial structure of these materials because of their multiphase character, dispersity and specific behavior in water. Clay is hydrated in an aqueous suspension to form adsorption layers of bound water; this results in the degradation of primary crystalline formations and in the dispersion of aggregates. The diffraction pattern taken after the precipitation and drying of a mass exhibited a decrease in the intensity of strong reflections from the crystalline phases of aluminum hydroxide and hydrated MgO. Calcination at 600°C resulted in the appearance of a γ-Al_2O_3 phase and, correspondingly, to the development of the surface. After calcination at 1150°C, the diffraction pattern became more complicated because of the superposition of lines due to a spinel structure. In this case, the dispersity of phases is difficult to determine, and this determination was performed for some of these phases using an individual line (see Table 3). The crystalline phases found correspond to a mixture of mullite and cordierite and an individual phase of corundum. The diffraction pattern of sample D3 after drying and calcination differs from the diffraction pattern of support D1 only in that spinel phases exhibit more pronounced lines, which is likely due to the high MgO content of the parent mass.

$\square$ $3Al_2O_3 \cdot 2SiO_2$
$\blacksquare$ $Mg_2Al_3 [AlSi_5O_{18}]$
$*$ $MgAl_2O_4$

1150°C

θ, deg

22   20   16   14

$\bullet$ AlOOH
$\circ$ $Mg_4 (OH)_2(CO_3)_3$
$\triangle$ $Al_2(OH)_4Si_2O_5$
$\blacktriangle$ SiO_2

100°C

θ, deg

20   16   12

X-ray diffraction patterns of sample D4 dried and calcined at 1150°C.

Spinel formation in sample D5 (identical to sample D1) occurred up to the formation of a crystalline phase of mullite (because of a lower homogeneity of the mixture and a weaker contact between crystallites). The mechanical strength of support D5 was low because a higher calcination temperature was required for sintering.

The phase composition of a support precipitated based on bentonite primarily depends on the concentration of the clay material. After precipitation and drying, the sample was X-ray amorphous because bentonite (montmorillonite clay) exhibits a variable lattice parameter distorted by the penetration of polar molecules between weakly bound layers. As a consequence, the sample was finely dispersed.

The diffraction pattern exhibits lines corresponding to boehmite, bentonite, and hydrated MgO phases (see the figure). At 600°C, highly dispersed phases were formed, as evidenced by the comparatively high specific surface area of the catalyst mass calcined at this temperature. The high dispersity of phases and the high homogeneity of mixtures in the course of synthesis were responsible for dramatic sintering at a high temperature; this resulted in spinel formation, and the specific surface area decreased.

A sample of another type was obtained by the precipitation of a support in an aqueous suspension of kieselguhr. The specific properties of kieselguhr did not allow us to reach a homogeneity of the medium characteristic of clay materials. In this case, the precipitated mass consisted of kieselguhr, MgO, and aluminum

hydroxide phases. After calcination at 1150°C, spinel formation occurred to a lesser degree; a portion of MgO remained unreacted to result in a decrease in the mechanical strength. In sample D2, the mullite phase was less pronounced. This allowed us to state that the cordierite structure was absent from this sample.

Samples D1 and D3–D6, which contained clay and bentonite, exhibited a cordierite–spinel-like structure. This structure is responsible for the physicomechanical properties of these supports.

The results of this study demonstrated that mullite–cordierite-like phases with framework structures were formed on the precipitation of boehmite in an aqueous suspension of bentonite or clay and in the presence of MgO at 1150°C. In a composite of the same composition prepared by mixing, the mullite phase was characterized by more intense reflections from a crystalline phase (dispersity of 170–190 Å). Consequently, with the use of a mixing technology, the temperatures of sintering and spinel formation should be higher than in precipitation because the medium is insufficiently homogeneous. High homogeneity, which takes place in the coprecipitation of initial components, is responsible for the fine dispersity of the precursor (i.e., a boehmite phase) and the low temperature of formation of a cordierite–mullite-like phase.

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