



# Article Synthesis of Vanadia-Mayenite Nanocomposites and Characterization of Their Structure, Morphology and Surface Sites

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**Abstract:** Calcium aluminates (CA) with a mayenite structure have attracted a growing interest during the last decades. The present paper reports the preparation of vanadia-mayenite composites performed via an impregnation of pure CA with ammonium vanadate solution. The properties of the prepared materials were explored by a low-temperature nitrogen adsorption/desorption technique, X-ray diffraction analysis, transmission electron microscopy, and spin probe method. As revealed, the addition of vanadium significantly affects the textural properties and the porous structure of mayenite. The blockage of micropores by vanadium species is supposed. The spin probe electron paramagnetic resonance technique based on the adsorption of 1,3,5-trinitrobenzene, phenothiazine, and diphenylamine has been applied to study the active sites on the surface of the composite samples. The results demonstrated an increase in the concentration of weak electron-acceptor sites when the vanadium loading was 10 wt%. X-ray diffraction analysis and transmission electron microscopy studies showed that the composites consist of few phases including mayenite, CaO, and calcium vanadates.

**Keywords:** mayenite; vanadia; nanocomposites; surface sites; textural and structural properties; morphology

## 1. Introduction

Calcium aluminates of different stoichiometry have been widely known for a long time, as they attract an attention of researchers and manufacturers as a component of cement mixtures [1]. The calcium aluminates of 12CaO·7Al<sub>2</sub>O<sub>3</sub> stoichiometry (usually labeled as C12A7) and the crystal structure of mayenite are of special interest. Such an increased attention to this class of materials is stimulated by their unique electrophysical and chemical properties discovered by the Prof. Hosono's group [2–5]. These materials possess a stable cationic framework  $[Ca_{24}Al_{28}O_{64}]^{4+}$  and a changeable anionic sublattice  $4 \cdot X^{-}$  [6]. Therefore, both the chemical and electrophysical properties of these aluminates can be easily changed in a wide range via an exchange of the X<sup>-</sup> anion. For instance, the X<sup>-</sup> anion can be H<sup>-</sup>, O<sup>-</sup>,  $O_2^-$ ,  $O^{2-}$ ,  $OH^-$ ,  $CI^-$ ,  $F^-$ , and  $e^-$ . In other words, materials with the mayenite structure are opposite version of zeolites, when the positive charge of the framework is compensated by the negative charge of the relatively mobile anionic sublattice, where the exact positions of the ions are not fixed [7]. These ions can occupy the positions from a huge number of the proper vacancies. This naturally leads to the polarization of the surface and the appearance of active sites with an increased chemical activity. Stabilization of the radical oxygen species over the mayenite lattice is of considerable interest for potential use as a catalyst or support for oxidation processes.

Most papers devoted to the preparation of mayenite-based materials have used a solid-phase synthesis method involving sintering at high temperatures. The main disadvantage of this approach is that the obtained mayenite samples are characterized by a low



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). specific surface area, and therefore they are poorly suited to be used as catalysts or their supports. Meza-Trujillo et al. have produced a high surface area mayenite of 74 m<sup>2</sup>·g<sup>-1</sup> using an assisted solution combustion synthesis from a mixture of calcium aluminates and aluminum in the presence of oxalic acid [8]. As we have reported recently, the highly dispersed calcium aluminates can be synthesized by the decomposition of mixed calcium and aluminum hydroxides covered with carbon [9,10]. This technique is also efficient for the preparation of a nanocrystalline mayenite with surface area of 60 m<sup>2</sup>·g<sup>-1</sup> and above, when the reaction between calcium oxide and aluminum hydroxide followed by the calcination in air was utilized [11].

The preparation of the mayenite-based composites is often performed via doping of pure mayenite with various cations, which introduction allows tuning the properties of C12A7 and widening the areas of its application [12,13]. For instance, the doping of mayenite with Tb makes it possible for applications in radiation measurements [14]. The introduction of Eu into the mayenite structure strongly affects its optical properties [15,16]. The resulting materials are shown to be attractive for application in X-ray radiation detection, solid-state lighting, and coating of the buildings' facades. Teusner et al. reported that the doping of mayenite with such cations as iron or nickel does not noticeably affect the oxygen surface exchange and oxygen tracer diffusion in mayenite [17]. On the other hand, Ruttanapun et al. have found that the substitution of Al<sup>3+</sup> sites in mayenite with Fe<sup>3+</sup> affected its thermal and optical properties [18]. Ni-doped mayenite exhibits promising catalytic properties for the steam reforming of raw syngas [19]. An increase in catalytic activity of the Cu-doped C12A7 systems is also reported in the literature [20,21].

Despite the mentioned works, the vanadia-mayenite composite systems are rarely studied. At the same time, V-containing TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MCM-41, etc., are widely applied in various industrially important processes including dehydrogenation of light hydrocarbons [22–26]. The oxidation state of vanadium is important for these processes since it defines the catalytic activity of the catalysts. In these terms, the introduction of vanadia into the mayenite structure is expected to stabilize the vanadium oxidation state and provide the long-term activity of the dehydrogenation catalyst.

Most of the oxide materials contain specific sites on their surface. The concentration of these sites can be very low, and the conventional characterization techniques are often not sensitive enough to measure them precisely. In this turn, a spin probe electron paramagnetic resonance (EPR) method is advantageous to explore such active sites on the surface of various types of materials [27–29]. Along with this, the spin probe EPR method is applicable for testing the highly active sites such as radical forms of oxygen [30,31], electron-acceptor sites capable to detaching electrons from aromatic spin probes [32–34], and electron-donor sites capable of releasing electrons to aromatic nitrocompounds [33,35]. As reported in the works mentioned, all of these sites play a crucial role in a number of chemical and catalytic reactions. It is worth noting that besides the electron-donor and electron-acceptor sites observed over the surface of many highly dispersed oxide materials, another exceptional type of site, probably of a radical nature, was discovered for mayenite. These sites generate nitroxyl radicals at the adsorption of diphenylamine [10].

The presence of the active oxygen radicals on the surface of mayenite activated in air stipulates an interest to prepare and explore the nanocrystalline mayenite modified by addition of vanadia. Vanadium species supported over various oxide carriers are intensively studied within the composition of catalysts for several processes [36–40]. Therefore, the present work is focused on the synthesis of the vanadia-containing composites based on calcium aluminate with a structure of mayenite. The prepared V/C12A7 samples were explored by a set of physicochemical methods for the first time. Here, the characterization data obtained by low-temperature nitrogen adsorption/desorption technique, X-ray diffraction analysis, and high-resolution transmission electron microscopy are reported. The active sites present on the surface of pure mayenite and vanadia-mayenite composites were investigated using a spin probe EPR technique. The optical properties of the samples, their reduction behavior as well as catalytic properties will be reported subsequently.

## 2. Materials and Methods

#### 2.1. Preparation of the Materials

In the present work, to obtain the highly dispersed mayenite in an aqueous medium, highly dispersed aluminum and calcium hydroxides were used as precursors [11]. Calcium hydroxide was prepared as follows.  $CaCO_3$  was decomposed via calcination in a muffle furnace to obtain CaO, which was then dissolved in an aqueous suspension containing pseudoboehmite taken in a required stoichiometric ratio. The typical procedures of the C12A7 synthesis include continuous stirring of the mixture for 10 h. As a result, the joint hydroxide of aluminum and calcium was formed. The sediment was filtered, dried at 110 °C, and calcined at 600 °C under the air atmosphere. The color of the prepared sample was white.

The composite V/C12A7 samples were prepared via an impregnation technique, as was recently described to obtain Ni/C12A7 system [19,41]. The solution of ammonium vanadate NH<sub>4</sub>VO<sub>3</sub> was used for the impregnation. Since NH<sub>4</sub>VO<sub>3</sub> is poorly soluble in water, the dissolution was performed at heating with the addition of ammonia. Thus, 200 mL of aqueous solution containing NH<sub>4</sub>VO<sub>3</sub> and NH<sub>4</sub>OH in a ratio of 1:5 was stirred at 70 °C until complete dissolution of the ammonium vanadate. Then, 57.5 mL or 115 mL of the obtained solution was added to the specimen of C12A7 (5 g) to prepare 5%V/C12A7 or 10%V/C12A7 samples (with respect to vanadium), respectively. The samples were stirred at 70 °C for 3 h, dried at 90 °C in the air for 24 h, and calcined at 600 °C for 6 h. The color of the prepared samples was light-yellow.

#### 2.2. Characterization of the Samples

The textural characteristics of the samples were studied by a low-temperature nitrogen adsorption/desorption technique. The adsorption/desorption isotherms were recorded using an automatic adsorption analyzer Autosorb-6B (Quantachrome Instruments, Boynton Beach, FL, USA). Before the measurements, the samples were treated by heating in a vacuum at absolute pressure of 1 Pa and temperature of 300 °C for 4 h. The calculations of the specific surface area (SSA), total pore volume (V<sub>pore</sub>), and average pore size (D<sub>av</sub>) were carried out using an ASWin 2.02 software (Quantachrome Instruments, Boynton Beach, FL, USA).

The active sites on the surface of the prepared materials were explored by an electron paramagnetic resonance technique using 1,3,5-trinitrobenzene (TNB), phenothiazine (PTZ), and diphenylamine (DPA) as spin probes. Before the adsorption of spin probes, the samples were activated by heating at 500 °C for 3 h. The adsorption of spin probes was performed from their solutions in toluene with a concentration of  $2 \cdot 10^{-2}$  M. The EPR spectra were obtained at room temperature using an ERS-221 spectrometer (Center of Scientific Instruments Engineering, Leipzig, Germany).

The phase composition of the samples was investigated by X-ray diffraction (XRD) analysis. The XRD patterns of the samples were recorded in a 20 range of 10–60° with a step of  $0.05^{\circ}$  and an accumulation time of 3 sec using a Bruker D8 diffractometer with CuK<sub> $\alpha$ </sub> radiation (Bruker AXS GmbH, Karlsruhe, Germany). The XRD analysis was made by the Rietveld method using the TOPAS software (Bruker AXS GmbH, Karlsruhe, Germany). The peak broadening in the XRD patterns was used to calculate the average sizes of the crystallites.

The structure and morphology of the samples were studied by a high-resolution transmission electron microscopy (HR TEM). An electron microscope ThemisZ (Thermo Fisher Scientific, Waltham, MA, USA) working with an accelerating voltage of 200 kV and a resolution limit of 0.07 nm. The images were recorded using a Ceta 16 CCD-camera (Thermo Fisher Scientific, Waltham, MA, USA). The elemental mapping was performed using an energy dispersive X-ray (EDX) spectrometer SuperX (Thermo Fisher Scientific, Waltham, MA, USA) with a semi-conductive Si-detector providing an energy resolution of 128 eV. The samples were deposited on the perforated carbon layer located on the copper or molybdenum grids using an ultrasonic disperser. This allowed achieving a uniform distribution of the particles on the surface of the supporting layer. The calculation of

interplanar distances was carried out using fast Fourier transform (FFT) patterns using Velox software (Thermo Fisher Scientific, Waltham, MA, USA) and Digital Micrograph

#### 3. Results

#### 3.1. Textural Properties of the Materials

(Gatan, Pleasanton, CA, USA).

The prepared pure mayenite and vanadia-containing composite samples were characterized by low-temperature nitrogen adsorption/desorption technique, and Figure 1 presents the adsorption/desorption isotherms for these materials. As seen, all the isotherms belong to Type II, according to the IUPAC classification [42,43]. The hysteresis loop observed for the pure C12A7 sample (Figure 1a) can be assigned to Type H1 [43,44]. At the same time, the addition of vanadium affects the textural properties of mayenite, and the hysteresis loops for the V/C12A7 samples are closer to Type H3. Therefore, it can be supposed that the vanadium species block the micropores of C12A7. The mesopores that remained accessible for the adsorbate are uniform in size and exhibit no percolation effects. Such mesopores are typical of the relatively small agglomerates chaotically oriented from each other.



**Figure 1.** Low-temperature nitrogen adsorption/desorption isotherms for C12A7 (**a**); 5%V/C12A7 (**b**); and 10%V/C12A7 (**c**) samples.

The textural characteristics of the samples are compared in Table 1. The pure mayenite possesses a relatively high surface area of 73  $\pm$  4 m<sup>2</sup>·g<sup>-1</sup>. The deposition of 5% V diminishes the SSA value by 21 m<sup>2</sup>·g<sup>-1</sup>. The total pore volume drops from 0.20  $\pm$  0.01 to 0.16  $\pm$  0.01 cm<sup>3</sup>·g<sup>-1</sup>, while average pore size grows from 11  $\pm$  0.6 to 13  $\pm$  0.7 nm. Here, the blockage of the micropores with vanadium species can be supposed. When the concentration of deposited vanadium is 10%, the SSA decreases by another 8 m<sup>2</sup>·g<sup>-1</sup>, but the pore volume remains the same. The average pore size for this sample reaches 16  $\pm$  0.01 nm. The pore size distributions for the samples are shown in Figure 2. As seen, the pure C12A7 sample is characterized by a narrow distribution within a pore size range of 5–30 nm. The vanadium addition affects the pore distribution, lowering the contribution of small pores. The distribution maximum shifts to the left, thus indicating that the mesopores undergo modification and narrowing. Along with this, a shoulder within a range of 30–200 nm has appeared. The appearance of macropores testifies towards the distortion of the mayenite structure and the possible local formation of the joint phases, presumably calcium vanadates.

Sample	SSA, $m^2 \cdot g^{-1}$	$V_{pore}$ , cm $^3 \cdot g^{-1}$	D <sub>av</sub> , nm
C12A7	$73 \pm 4$	$0.20\pm0.01$	$11\pm0.6$
5%V/C12A7	$52 \pm 3$	$0.16\pm0.01$	$13\pm0.7$
10%V/C12A7	$40\pm 2$	$0.16\pm0.01$	$16\pm0.8$

Table 1. Textural characteristics of C12A7, 5%V/C12A7, and 10%V/C12A7 samples.



Figure 2. Pore size distributions for C12A7, 5%V/C12A7, and 10%V/C12A7 samples.

## 3.2. EPR Study

As recently reported, the spin probe EPR technique can be efficiently applied for the characterization of various active sites on the surface of oxide supports [35,45,46]. It should be noted that all the spin probes used for the examination of such sites by means of EPR contain nitrogen atoms. Therefore, their EPR spectra in the adsorbed state represent three-component signals with hyperfine splitting at one nitrogen atom. The spectra observed after the adsorption of TNB over C12A7 are close to the spectrum of the 1,3,5-trinitrobenzene radical anions, which were recently registered over alumina [35]. As seen from Figure 3a, a hindered triplet signal with g = 2.005 is observed. The hyperfine splitting constant of  $A_{zz} = 26.5$  G does not practically change after the deposition of vanadium. This testifies towards the similarity of the electron-donor sites present on the surface of aluminum oxide and C12A7 samples, pure and vanadia-containing ones. The concentration of the electron-donor sites on the C12A7 surface capable to give an electron to the TNB molecule is estimated to be  $0.68 \cdot 10^{18}$  g<sup>-1</sup> (Table 2). The introduction of 5% vanadium does not have any effect on this parameter, while for the 10%V/C12A7 sample, the concentration of the active sites is slightly reduced.

**Table 2.** Concentration of the active sites  $(10^{18} \text{ g}^{-1})$  over C12A7 and V/C12A7 samples measured by a spin probe EPR technique.

Spin Probe –	Sample		
	C12A7	5%V/C12A7	10% V/C12A7
Diphenylamine	$0.71\pm0.14$	$0.64\pm0.13$	$0.97\pm0.20$
Phenothiazine	$0.93\pm0.19$	$0.92\pm0.18$	$1.33\pm0.27$
1,3,5-Trinitrobenzene	$0.68\pm0.14$	$0.69\pm0.12$	$0.58\pm0.12$

(c-1) (a-1) (b-1) (c-2) (a-2) (b-2) **י**g ⁺g<sub>e</sub> 'g\_ 3 3 3 3400 3350 3400 3450 3500 3350 3450 3500 3300 3350 3400 3450 Magnetic field, G Magnetic field, G Magnetic field, G

**Figure 3.** Spin probes and EPR spectra observed after their adsorption over C12A7 (1); 5%V/C12A7 (2); and 10%V/C12A7 (3) samples activated at 500 °C: 1,3,5-trinitrobenzene (**a**); phenothiazine (**b**); and diphenylamine (**c**). Designation of the atoms: carbon (grey); hydrogen (white); nitrogen (blue); oxygen (red); sulfur (yellow).

It was found that the sites able to ionize perylene, which are present in a noticeable amount over the alumina surface, are absent in the case of mayenite. At the same time, the weaker electron-acceptor sites ionizing phenothiazine were found on the surface of C12A7 and V/C12A7 samples. Note that the ionization potential of PTZ is 6.73 eV, which allows applying it for the testing of weak electron-acceptor sites [47,48]. For the pure and vanadia-containing C12A7 samples, the adsorption of PTZ gives a triplet signal with a hyperfine splitting constant of  $A_{zz} = 18$  G, which corresponds to the PTZ radical cation (Figure 3b).

The concentration of the weak electron-acceptor sites measured after the adsorption of PTZ on the surface of pure C12A7 was found to be 1.5 times higher than the concentration of the electron-donor sites on its surface (Table 2). The addition of 5% V does not affect the concentration of these sites, while an increase up to  $1.33 \cdot 10^{18}$  g<sup>-1</sup> is observed in the case of 10%V/C12A7 sample (Table 1).

The ionization potential of DPA is also relatively low. Depending on the estimation techniques, it lies in a range of 7.35–7.48 eV [49]. This allows the DPA molecules to ionize over weak electron-acceptor sites, which exist on the surface of several acidic materials, with the formation of radical cations. However, it is known that DPA forms quite stable diphenyloxyl nitroxyl radicals in the solution in the presence of peroxides [50]. Supposedly, this happens due to the reaction of DPA with hydroxyls formed at the decomposition of peroxides.

The spectrum observed after the adsorption of DPA on the samples of pure mayenite and vanadia-mayenite composites is represented by a triplet with a constant  $A_{zz} = 16$  G. This triplet can be attributed to the diphenyloxyl nitroxyl radicals adsorbed on the surface of the samples (Figure 3c). The formation of the radicals testifies towards the existence of a noticeable concentration of radicals on the surface of the highly dispersed mayenite samples, which are capable of detaching the hydrogen atom from the nitrogen atom of the spin probe molecule. These surface radicals can be O<sup>-</sup>, OH or O<sub>2</sub><sup>-</sup>. The introduction of 10% V slightly increases the concentration of such sites (Table 2).

#### 3.3. XRD Study

Powder X-ray diffraction analysis is more informative in terms of the possible formation of the vanadium-mayenite joint phases. Figure 4a shows the XRD patterns for the C12A7 and 10%V/C12A7 samples. The pattern for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is given for comparison. In the case of pure C12A7 sample, the nanocrystalline mayenite phase predominates and reaches ~70 wt%. The residual phase is CaO. The average sizes (D<sub>c</sub>) of the mayenite and CaO crystallites are of ~15 and ~12 nm, respectively. The dashed line illustrates the reflection position for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase, which also appears in the patterns of the studied samples. The presence of the simple oxides (CaO, Al<sub>2</sub>O<sub>3</sub>) is supposedly connected with their incomplete reaction during the synthesis procedures.



**Figure 4.** Powder XRD patterns of C12A7 and 10%V/C12A7 samples (**a**); XRD analysis of 10%V/C12A7 sample (**b**).

The performed XRD analysis of 10%V/C12A7 sample (Figure 4b) has revealed that the pattern, in addition to the reflections assigned to nanocrystalline mayenite (D<sub>c</sub>~14 nm), CaO ( $D_c \sim 9$  nm), and Al<sub>2</sub>O<sub>3</sub>, contains the reflections corresponding to calcium vanadates  $Ca_2V_2O_7$  (D<sub>c</sub>~20 nm) and  $Ca_3(VO_4)_2$  (D<sub>c</sub>~20 nm). It is important to note that the intensities of the reflections assigned to mayenite and CaO are decreased if compared with pure C12A7. The weight ratio was quantitatively estimated to be 50/14/24/12 for the phases mayenite/CaO/Ca<sub>2</sub>V<sub>2</sub>O<sub>7</sub>/Ca<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>, respectively. Therefore, it can be supposed that calcium vanadates are predominantly formed due to the interaction of CaO with NH<sub>4</sub>VO<sub>3</sub>. Mayenite can also participate in the vanadates formation, but its contribution is significantly lower. Such a conclusion is evident from the changes in weight ratio as from the observed decrease in average size of the crystallites. Thus, the mayenite crystallites are just slightly diminished in size from 15 to 14 nm, while the size of the CaO nanoparticles is changed from 12 to 9 nm. Most likely, the impregnation of mayenite with an aqueous solution of  $NH_4VO_3$  leads to the modification of mayenite structure with vanadium ions, which is seen as an increase in the lattice parameter from 12.004(2) Å to 12.052(3) Å. On the other hand, the formation of larger particles of calcium vanadates can be responsible for the changes in textural characteristics, described in Section 3.1.

#### 3.4. TEM Study

According to the HR TEM and EDX data (Figure 5), the vanadia-mayenite composite 10%V/C12A7 consists of a mixture of oxide particles of various morphologies. First of all, the laminated particles consisting of calcium and vanadium cations should be mentioned. The stoichiometric formula of these particles is estimated as Ca<sub>4</sub>V<sub>2</sub>O<sub>9</sub>, which corresponds to a mixture of the CaO and Ca<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> phases. The size of this structural type is varied in a wide range from a few tens nm to a few microns. The crystallites composing these particles are located chaotically, thus forming a porous structure with a pore size of about 1 nm. The second type of the particle is also of a platelet shape and similar size. However, the chemical composition calculated from the EDX data gives the cation ratio Ca/Al of 34/20, which is close to the mayenite composition (Figure 5b). The third type of particle is represented, according to the EDX results, by aluminum oxide (Figure 5c). Their size lies in a range from 100 nm to few microns. The primary crystallites composing these particles are of ~10 nm in size. Being agglomerated, they also form a porous structure with the pores of 1–5 nm in size. The smaller particles of the former phases are located on the surface of the aggregated particles.

The analysis of the interplanar distances (Figure 6) revealed that the vanadiumcontaining particles can be assigned to the  $Ca_4V_2O_9$  phase (#PDF 48-538). These wellcrystallized particles contain pores of 1–3 nm in diameter chaotically distributed on the surface (Figure 5d). The EDX elemental mapping presented in Figure 7 shows the uniform distribution of aluminum, calcium and vanadium within the particle of vanadiamayenite composite.



**Figure 5.** HR TEM images of 10%V/C12A7 sample: (**a**,**b**) mayenite particles; (**c**) alumina-rich particles; (**d**) calcium vanadate particle.



**Figure 6.** The FFT patterns of 10%V/C12A7 sample: (**a**) mayenite particle shown in Figure 5a; (**b**) calcium vanadate particle shown in Figure 5d.



Figure 7. TEM image (a) and EDX elemental mapping (b–e) of the vanadia-mayenite composite particle.

#### 4. Conclusions

The textural, surface, and structural properties of the vanadia-mayenite composites are reported here for the first time. It was found that the introduction of vanadium changes the porous structure of mayenite. The micropores are being blocked with vanadium species and the hysteresis loop observed in the low-temperature nitrogen adsorption/desorption isotherms transforms from Type H1 to Type H3. The SSA value decreases from  $73 \pm 4 \text{ m}^2 \cdot \text{g}^{-1}$  for pure mayenite to  $40 \pm 2 \text{ m}^2 \cdot \text{g}^{-1}$  for 10%V/C12A7 composite. The surface properties, which are defined by the presence of various active sites (electron-donor, electron-acceptor, etc.), are also slightly affected by the addition of vanadium. Thus, the adsorption of phenothiazine and diphenylamine served as spin probes for the EPR detection of weak electron-acceptor sites has revealed an increased concentration of these sites from  $(0.71 \pm 0.14) \cdot 10^{18}$  g<sup>-1</sup> to  $(0.97 \pm 0.20) \cdot 10^{18}$  g<sup>-1</sup> and from  $(0.93 \pm 0.19) \cdot 10^{18}$  g<sup>-1</sup> to  $(1.33 \pm 0.27) \cdot 10^{18}$  g<sup>-1</sup>, respectively, when the V loading was 10 wt%. The XRD studies showed that the V/C12A7 samples contain nanocrystalline mayenite particles of ~14 nm in size, CaO particles of ~9 nm in size, and Al<sub>2</sub>O<sub>3</sub>. Additionally, the reflections corresponding to calcium vanadates  $Ca_2V_2O_7$  and  $Ca_3(VO_4)_2$  were registered. The average particle size of calcium vanadates was found to be ~20 nm. The exploration of the samples by the high-resolution TEM combined with EDX elemental mapping confirms the presence of the mentioned phases and illustrates their uniform distribution within the material.

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## References

- Ideker, J.H.; Scrivener, K.L.; Fryda, H.; Touzo, B. Calcium Aluminate Cements. In *Lea's Chemistry of Cement and Concrete*; Butterworth-Heinemann: Oxford, UK, 2019; pp. 537–584.
- Hayashi, K.; Matsuishi, S.; Kamiya, T.; Hirano, M.; Hosono, H. Light-induced conversion of an insulating refractory oxide into a persistent electronic conductor. *Nature* 2002, 419, 462–465. [CrossRef] [PubMed]
- Li, Q.; Hosono, H.; Hirano, M.; Hayashi, K.; Nishioka, M.; Kashiwagi, H.; Torimoto, Y.; Sadakata, M. High-intensity atomic oxygen radical anion emission mechanism from 12CaO·7Al<sub>2</sub>O<sub>3</sub> crystal surface. *Surf. Sci.* 2003, 527, 100–112. [CrossRef]
- 4. Yang, S.; Kondo, J.N.; Hayashi, K.; Hirano, M.; Domen, K.; Hosono, H. Partial oxidation of methane to syngas over promoted C12A7. *Appl. Catal. A Gen.* 2004, 277, 239–246. [CrossRef]
- Kitano, M.; Inoue, Y.; Yamazaki, Y.; Hayashi, F.; Kanbara, S.; Matsuishi, S.; Yokoyama, T.; Kim, S.-W.; Hara, M.; Hosono, H. Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store. *Nat. Chem.* 2012, *4*, 934–940. [CrossRef] [PubMed]
- 6. Tang, X.; Kuehster, A.E.; DeBoer, B.A.; Preston, A.D.; Ma, K. Enhanced thermionic emission of mayenite electride composites in an Ar glow discharge plasma. *Ceram. Int.* 2021, 47, 16614–16631. [CrossRef]
- Miyakawa, M.; Murata, H.; Imai, M. Direct synthesis of H<sup>-</sup>-encaged 12CaO·7Al<sub>2</sub>O<sub>3</sub> crystals by high-pressure processes. *Ceram. Int.* 2019, 45, 16028–16031. [CrossRef]
- 8. Meza-Trujillo, I.; Devred, F.; Gaigneaux, E.M. Production of high surface area mayenite (C12A7) via an assisted solution combustion synthesis (SCS) toward catalytic soot oxidation. *Mater. Res. Bull.* **2019**, *119*, 110621. [CrossRef]
- 9. Volodin, A.M.; Zaikovskii, V.I.; Kenzhin, R.M.; Bedilo, A.F.; Mishakov, I.V.; Vedyagin, A.A. Synthesis of nanocrystalline calcium aluminate C12A7 under carbon nanoreactor conditions. *Mater. Lett.* **2017**, *189*, 210–212. [CrossRef]
- 10. Volodin, A.M.; Bedilo, A.F.; Stoyanovskii, V.O.; Zaikovskii, V.I. High-temperature synthesis of finely dispersed oxide materials and C12A7:e electrides in carbon nanoreactor conditions. *Nanosyst. Phys. Chem. Math.* **2018**, *9*, 558–567. [CrossRef]
- 11. Kapishnikov, A.V.; Kenzhin, R.M.; Koskin, A.P.; Volodin, A.M.; Geydt, P.V. Mayenite synthesis from hydroxide precursors: Structure formation and active sites on its surface. *Materials* **2022**, *15*, 778. [CrossRef]
- 12. Khan, K.; Tareen, A.K.; Aslam, M.; Thebo, K.H.; Khan, U.; Wang, R.; Shams, S.S.; Han, Z.; Ouyang, Z. A comprehensive review on synthesis of pristine and doped inorganic room temperature stable mayenite electride,  $[Ca_{24}Al_{28}O_{64}]^{4+}(e^{-})_4$  and its applications as a catalyst. *Prog. Solid State Chem.* **2019**, *54*, 1–19. [CrossRef]
- Huang, J.; Valenzano, L.; Sant, G. Framework and channel modifications in mayenite (12CaO·7Al<sub>2</sub>O<sub>3</sub>) nanocages By cationic doping. *Chem. Mater.* 2015, 27, 4731–4741. [CrossRef]
- 14. Kumamoto, N.; Nakauchi, D.; Kato, T.; Okada, G.; Kawaguchi, N.; Yanagida, T. Photoluminescence, scintillation and thermallystimulated luminescence properties of Tb-doped 12CaO·7Al<sub>2</sub>O<sub>3</sub> single crystals grown by FZ method. *J. Rare Earths* **2017**, 35, 957–963. [CrossRef]
- 15. Kumaresh, T.; Awin, E.W.; Bhaskar, L.K.; Djordjevic, M.P.; Matović, B.; Kumar, R. Combustion synthesis of luminescent Eu-doped single phase Mayenite. *J. Solid State Chem.* **2021**, 302, 122420. [CrossRef]
- 16. Duan, J.; Liu, Y.; Pan, X.; Gu, Y.; Zheng, X.; Li, W.; Wang, W.; Wang, C.; Yu, J. Transparency, photoluminescence and X-ray luminescence study of Eu<sup>3+</sup> doped mayenite glass. *Mater. Lett.* **2016**, *173*, 102–106. [CrossRef]
- 17. Teusner, M.; De Souza, R.A.; Krause, H.; Ebbinghaus, S.G.; Martin, M. Oxygen transport in undoped and doped mayenite. *Solid State Ion.* **2016**, *284*, 25–27. [CrossRef]
- Ruttanapun, C.; Srepusharawoot, P.; Maensiri, S. Effect of Fe<sup>3+</sup>-doped Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> cement on optical and thermal properties. *Chin. J. Phys.* 2018, 56, 252–260. [CrossRef]
- 19. Savuto, E.; Di Carlo, A.; Gallucci, K.; Natali, S.; Bocci, E. Characterization and performance analysis of an innovative Ni/Mayenite catalyst for the steam reforming of raw syngas. *Fuel* **2017**, *194*, 348–356. [CrossRef]
- Salasin, J.R.; Schwerzler, S.E.A.; Koehler, M.R.; Keffer, D.J.; Rawn, C.J. The effect of process parameters on the amorphous citrate sol-gel synthesis of Cu-doped Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. *Materialia* 2018, 4, 466–477. [CrossRef]
- Meza-Trujillo, I.; Mary, A.; Pietrzyk, P.; Sojka, Z.; Gaigneaux, E.M. Nature and role of Cu(II) species in doped C12A7 catalysts for soot oxidation. *Appl. Catal. B Environ.* 2022, 316, 121604. [CrossRef]

- 22. Balcaen, V.; Sack, I.; Olea, M.; Marin, G.B. Transient kinetic modeling of the oxidative dehydrogenation of propane over a vanadia-based catalyst in the absence of O<sub>2</sub>. *Appl. Catal. A Gen.* **2009**, *371*, 31–42. [CrossRef]
- Rodemerck, U.; Sokolov, S.; Stoyanova, M.; Bentrup, U.; Linke, D.; Kondratenko, E.V. Influence of support and kind of VO species on isobutene selectivity and coke deposition in non-oxidative dehydrogenation of isobutane. *J. Catal.* 2016, 338, 174–183. [CrossRef]
- Rodemerck, U.; Stoyanova, M.; Kondratenko, E.V.; Linke, D. Influence of the kind of VO<sub>x</sub> structures in VO<sub>x</sub>/MCM-41 on activity, selectivity and stability in dehydrogenation of propane and isobutane. *J. Catal.* 2017, 352, 256–263. [CrossRef]
- 25. Hu, P.; Lang, W.-Z.; Yan, X.; Chen, X.-F.; Guo, Y.-J. Vanadium-doped porous silica materials with high catalytic activity and stability for propane dehydrogenation reaction. *Appl. Catal. A Gen.* **2018**, 553, 65–73. [CrossRef]
- Shan, Y.-L.; Zhao, W.-T.; Zhao, S.-L.; Wang, X.-X.; Sun, H.-L.; Yu, W.-L.; Ding, J.-W.; Feng, X.; Chen, D. Effects of alumina phases on the structure and performance of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts in non-oxidative propane dehydrogenation. *Mol. Catal.* 2021, 504, 111466. [CrossRef]
- García, H.; Roth, H.D. Generation and reactions of organic radical cations in zeolites. *Chem. Rev.* 2002, 102, 3947–4008. [CrossRef]
- Chiesa, M.; Giamello, E.; Che, M. EPR Characterization and reactivity of surface-localized inorganic radicals and radical ions. *Chem. Rev.* 2009, 110, 1320–1347. [CrossRef]
- 29. Golubeva, E.N.; Chumakova, N.A. Spin probe method for diagnostics of polyester porous matrixes formed in supercritical carbon dioxide (Review). *Russ. J. Phys. Chem. B* 2020, *13*, 1088–1094. [CrossRef]
- Anpo, M.; Costentin, G.; Giamello, E.; Lauron-Pernot, H.; Sojka, Z. Characterisation and reactivity of oxygen species at the surface of metal oxides. J. Catal. 2021, 393, 259–280. [CrossRef]
- 31. Malykhin, S.E.; Volodin, A.M.; Bedilo, A.F.; Zhidomirov, G.M. Generation of O<sup>-</sup> radical anions on MgO surface: Long-distance charge separation or homolytic dissociation of chemisorbed water? *J. Phys. Chem. C* 2009, *113*, 10350–10353. [CrossRef]
- 32. Bedilo, A.F.; Volodin, A.M. Radical cations of aromatic molecules with high ionization potentials on the surfaces of oxide catalysts: Formation, properties, and reactivity. *Kinet. Catal.* **2009**, *50*, 314–324. [CrossRef]
- Bedilo, A.F.; Shuvarakova, E.I.; Rybinskaya, A.A.; Medvedev, D.A. Characterization of electron-donor and electron-acceptor sites on the surface of sulfated alumina using spin probes. J. Phys. Chem. C 2014, 118, 15779–15794. [CrossRef]
- 34. Shuvarakova, E.I.; Bedilo, A.F.; Chesnokov, V.V.; Kenzhin, R.M. Dehydrochlorination of 1-chlorobutane over nanocrystalline MgO: The role of electron-acceptor sites. *Top. Catal.* **2018**, *61*, 2035–2041. [CrossRef]
- Medvedev, D.A.; Rybinskaya, A.A.; Kenzhin, R.M.; Volodin, A.M.; Bedilo, A.F. Characterization of electron donor sites on Al<sub>2</sub>O<sub>3</sub> surface. *Phys. Chem. Chem. Phys.* 2012, 14, 2587–2598. [CrossRef] [PubMed]
- 36. Zhu, C.; Chen, S.; Pan, D.; Cui, X.; Qiao, Y.; Li, R. Ordered mesoporous alumina-supported vanadium oxides as an efficient catalyst for ethylbenzene dehydrogenation to styrene with CO<sub>2</sub>. *Catal. Commun.* **2018**, *115*, 12–16. [CrossRef]
- 37. Held, A.; Kowalska-Kuś, J.; Janiszewska, E.; Jankowska, A.; Nowińska, K. Epoxidation of propane with oxygen and/or nitrous oxide over silica-supported vanadium oxide. *J. Catal.* **2021**, 404, 231–243. [CrossRef]
- 38. Huang, Z.; Ma, S.; Qu, B.; Li, D.; Zhou, R. Migration and oxidation of vanadium atom and dimer supported on anatase TiO<sub>2</sub>(101) surface. *Appl. Surf. Sci.* **2021**, *565*, 150517. [CrossRef]
- Rajitha, P.; Mahesh Kumar, P.; Mallesh, D.; Lingaiah, N. Understanding the role of Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> mixed oxides as support for vanadium catalysts for the selective ammoxidation of o-chlorotoluene to o-chlorobenzonitrile. *Mol. Catal.* 2021, *515*, 111885. [CrossRef]
- 40. Fernandes, A.; Ribeiro, M.F.; Lourenço, J.P. Conversion of glycerol over vanadium supported beta zeolite: Role of acidity and alkali cations. *Microporous Mater.* **2022**, *329*, 111536. [CrossRef]
- Di Carlo, A.; Borello, D.; Sisinni, M.; Savuto, E.; Venturini, P.; Bocci, E.; Kuramoto, K. Reforming of tar contained in a raw fuel gas from biomass gasification using nickelmayenite catalyst. *Int. J. Hydrogen Energy* 2015, 40, 9088–9095. [CrossRef]
- 42. Thommes, M. Physical adsorption characterization of nanoporous materials. Chem. Ing. Tech. 2010, 82, 1059–1073. [CrossRef]
- 43. Cychosz, K.A.; Thommes, M. Progress in the physisorption characterization of nanoporous gas storage materials. *Engineering* **2018**, *4*, 559–566. [CrossRef]
- Sing, K.S.W.; Williams, R.T. Physisorption hysteresis loops and the characterization of nanoporous materials. *Adsorpt. Sci. Technol.* 2004, 22, 773–782. [CrossRef]
- Vedyagin, A.A.; Volodin, A.M.; Kenzhin, R.M.; Stoyanovskii, V.O.; Rogov, V.A.; Kriventsov, V.V.; Mishakov, I.V. The role of chemisorbed water in formation and stabilization of active sites on Pd/Alumina oxidation catalysts. *Catal. Today* 2018, 307, 102–110. [CrossRef]
- Vedyagin, A.A.; Volodin, A.M.; Stoyanovskii, V.O.; Kenzhin, R.M.; Plyusnin, P.E.; Shubin, Y.V.; Mishakov, I.V. Effect of alumina phase transformation on stability of low-loaded Pd-Rh catalysts for CO oxidation. *Top. Catal.* 2016, 60, 152–161. [CrossRef]
- 47. Luchez, F.; Carré, S.; Moissette, A.; Poizat, O. Sorption and spontaneous ionization of phenothiazine within channel type zeolites: Effect of the confinement on the electron transfers. *RSC Adv.* **2011**, *1*, 341–350. [CrossRef]
- 48. Shaydyuk, Y.; Turrell, S.; Moissette, A.; Hureau, M.; Gomza, Y.; Klepko, V.; Lebovka, N. New phenothiazine–laponite hybrid systems: Adsorption and ionization. *J. Mol. Struct.* **2014**, *1056–1057*, 1–6. [CrossRef]

- 49. Freitas, V.L.S.; Gomes, J.R.B.; Liebman, J.F.; Ribeiro da Silva, M.D.M.C. Energetic and reactivity properties of 9,10-dihydroacridine and diphenylamine: A comparative overview. *J. Chem. Thermodyn.* **2017**, *115*, 276–284. [CrossRef]
- 50. Ilyina, E.V.; Gerus, Y.Y.; Cherepanova, S.V.; Bedilo, A.F. Synthesis of C12A7 calcium aluminate aerogels. *Mater. Lett.* **2021**, 293, 129699. [CrossRef]