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COMPARATIVE STUDY ON PRODUCTION METHODS OF MAYENITE CATALYST SUPPORTS

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ABSTRACT – *The interesting catalytic properties of mayenite, related to its particular crystal structure, makes it suitable for use in catalyst synthesis. The objective of this study is to evaluate different preparation methods of a mayenite catalyst support. Three methods were studied (solid mixing in a high energy mill, solid mixing in a conventional ball mill and hydrothermal method) and samples were characterized by phase identification (XRD) and textural properties. The results showed that single phase mayenite (S_{BET} 30.3 m²/g) can be produced by high energy milling method. On the other hand, mayenite with a specific surface area of 57.0 m²/g can be produced by the simple method of conventional ball milling. However, other phases were present in the sample. Mayenite produced was found to be promising for application as support on catalyst production.*

1. INTRODUCTION

The mineral mayenite was originally reported from the Eifel volcanic complex in Germany and was named due to the place of its discovery, Mayen (Germany). It is one of the intermediate phases of the CaO-Al₂O₃ binary system, stoichiometrically represented as Ca₁₂Al₁₄O₃₃. Mayenite was historically studied as a common phase present in Portland cement and has recently enjoyed renewed research interest due to the discovery of oxygen mobility, ionic conductivity (SCHMIDT et al., 2014) and sorbent properties (CUCCINIELLO et al., 2017). Mayenite has also been used as catalyst support for tar cracking in biomass gasification (LI et al., 2009). According to Schmidt et al. (2014), mayenite presents a quite uncommon crystal structure that may be described as some kind of anti-zeolite, as it forms positively charged cage-like structures, partially occupied by anions. Mayenite, also written as C12A7 (12CaO·7Al₂O₃) is a complex oxide of Ca and Al whose stoichiometric cubic unit cell is expressed as [Ca₂₄Al₂₈O₆₄]⁴⁺·2O²⁻ where 64 of the 66 oxygen ions per unit cell are fixed in a Ca–Al–O framework forming 12 “cages”, while the other two oxygen ions are distributed within the cages (LI et al., 2009). These oxygen atoms are often described as “free” or “extra-framework” oxygen, as they are only lightly bound (SCHMIDT et al., 2014).

The interesting catalytic properties of mayenite are related to its particular crystal structure and extra-framework oxygen. The latter, highly reactive species are responsible for migrating to the active site of catalyst (e.g. Ni, Co and Pt) and gasifying the deposited carbon



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to CO, preserving the deactivation of catalyst due to carbon deposition. Furthermore, a study performed by Li et al. (2009) showed that the free oxygen in the structure of the catalysts can be replaced by sulfur, extending the catalyst life time in the presence of H₂S. Despite its suitable catalytic properties, the conventional method of mayenite production (solid state reaction) needs high reaction temperatures and long reaction times. Moreover, the high temperatures used lead to a drastic reduction in the specific surface area of mayenite. Therefore it is crucial to understand the influence of the production method in the final properties of mayenite. The objective of this study is to evaluate different preparation methods of a mayenite catalyst support by means of its textural properties and phase identification.

2. MATERIALS AND METHODS

Mayenite was produced from Ca(OH)₂ (purity > 95%) and Al(OH)₃ (purest) bought from Cinética Reagents & Solutions. Initially, the precursors were mixed in stoichiometric ratio (6:7) and the mixture was used in the different production methods described in the following sections.

2.1. Solid Mixing Method in a High Energy Mill

In the high energy mill method, 13 g of the precursors were grounded in a high energy planetary ball mill (Retsch, Emax) for 10 min at a grinding rate of 1000 rpm. Another sample was produced in the high energy mill under the same conditions, except the grinding rate defined as 400 rpm.

2.2. Solid Mixing Method in a Conventional Ball Mill

A conventional stainless steel ball mill was used to mix about 350 g of precursors at a grinding rate of 47 rpm. The mixture was kept for 24 h.

2.3. Hydrothermal Method

Mayenite was prepared following the method proposed by Cucciniello et al. (2017). According to the method, 10 g of precursors were added to 100 mL of distilled water and grounded under magnetic stirring for 4h at 25 °C. Then, the mixture was placed in an autoclave at 150 °C for 5h. The obtained solid was filtered and dried at 105 °C overnight.

After the procedures, samples from high energy mill method (400 and 1000 rpm), conventional ball mill method and hydrothermal method were calcined at 1000 °C in air for 4h. Samples were named HEM400, HEM1000, CBM and HM, respectively.

2.4. Characterization

X-ray powder diffraction (XRD): Samples were investigated by X-ray diffraction analysis (Shimadzu X-ray diffractometer, XRD 6000) in the 2θ range of 5-90° with the resolution of 0.05°.

N₂ adsorption isotherms: Specific surface area, total pore volume and average pore diameter were characterized by N₂ adsorption at 77 K in a Surface Area and Pore Size Analyzer (Quantachrome, Nova 1200). Prior to analysis, samples were outgassed under vacuum at 380 °C for 20 h.

3. RESULTS AND DISCUSSION

The XRD patterns of the materials prepared by the described methods are shown in Figure 1. It is clear from the figure that mayenite was successfully produced by the 4 methods studied. In addition, sample HEM1000 presented only Ca₁₂Al₁₄O₃₃ phase while CaO and CaAl₄O₇ phases were observed in the other samples. Furthermore, mayenite produced by HEM1000 method presented the highest crystallinity according to the highest intensity of the peaks (LI et al., 2009). The high concentration of CaO observed in the HEM400 sample, indicates that the lowest grinding rate was not appropriate.

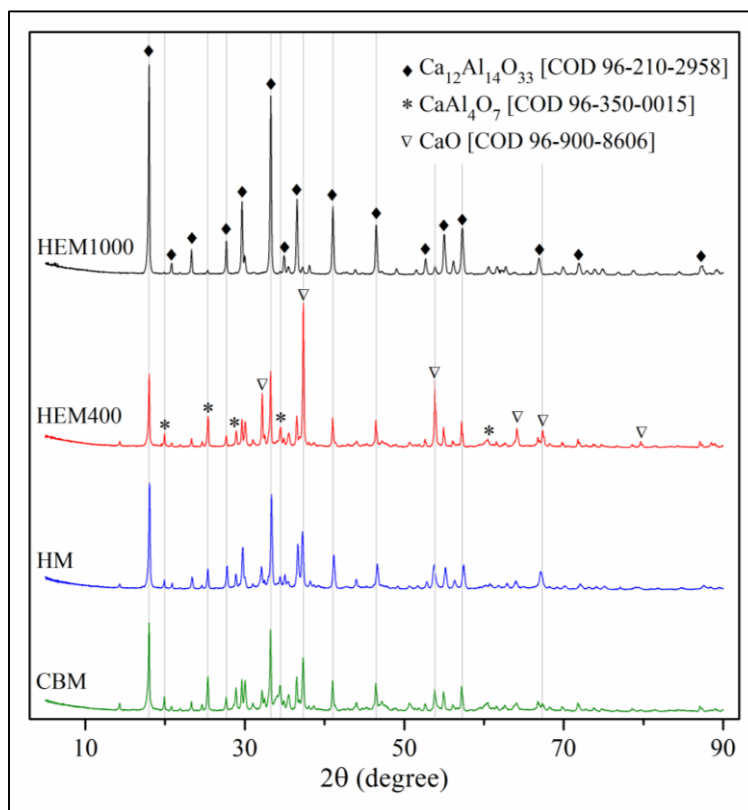


Figure 1 – XRD patterns of mayenite from different preparation methods

The CaO phase (pure Ca) and CaAl₄O₇ phase (Al-rich phase) observed in the samples may be an indicative of insufficient mixing of reagents. According to Iftekhar et al. (2008), CaAl₄O₇ is a more unreactive phase of Ca-Al-O system. Therefore, once formed, it is difficult to continue reacting to the formation of Ca₁₂Al₁₄O₃₃. The presence of CaO was also reported by Ozawa et al. (2011) in a mayenite produced by the sol-gel method and calcined at 900 °C. Textural properties of mayenite samples are presented in Table 1. It is well known that higher surface areas are related to larger pore volumes and/or smaller pore diameters. HEM1000 presented the lowest surface area due to the fact that the sample had lower pore volume and



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its pores had a larger average diameter, as can be observed in Table 1.

Table 1 – Textural properties of mayenite from different preparation methods

Samples	S_{BET} (m ² /g)	V_{P} (cm ³ /g)	D_{P} (nm)
HEM1000	30.3	0.065	8.6
HEM400	50.9	0.079	6.2
CBM	57.0	0.109	7.9
HM	40.5	0.079	7.6

The larger surface area (57.0 m²/g) obtained for CBM can be attributed mainly to its high total pore volume. According to Ozawa et al. (2011), catalysts usually present specific surface area in the range of 30 to 130 m²/g. Thus, in view of the surface area, mayenite samples produced in this work can be used as support for the production of catalysts for gasification processes.

4. CONCLUSIONS

Mayenite (C₁₂Al₁₄O₃₃) was successfully synthesized by different methods. Single phase mayenite with 30.3 m²/g was produced by high energy milling method with a short mixing time (10 min). The simple method of conventional ball milling allowed mayenite production, however other phases (i.e. CaO, CaAl₄O₇) were present in the synthesized sample. Finally, the four studied methods proved to be suitable for the production of mayenite support with different qualities for use in catalyst synthesis.

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