Natural magnesium oxide (MgO) catalysts: A cost-effective sustainable alternative to acid zeolites for the *in situ* upgrading of biomass fast pyrolysis oil

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ABSTRACT

The thermal and catalytic fast pyrolysis of biomass aims at the production of pyrolysis oil (bio-oil), which can be utilized as a source of chemicals or as a bio-crude for the production of hydrocarbon fuels. We investigated low-cost, naturally derived basic MgO materials as catalysts for the catalytic fast pyrolysis of lignocellulosic biomass as alternatives to classical acidic zeolite catalysts. The MgO catalysts were produced from natural magnesite mineral without any significant treatment besides calcination, crushing and sieving. Their structure, composition, porosity, morphology and surface properties were thoroughly examined by XRD, XRF, N_2 porosimetry, SEM, TEM, TPD-CO_2 and TPD-NH_3. The physicochemical characteristics of the MgO catalysts depended mainly on the different production conditions (duration and temperature of calcination). Despite their negligible acidity, the MgO catalysts effectively reduced the oxygen content of the produced bio-oil and exhibited similar or even better performance compared to that of an industrial ZSM-5 catalyst formulation (*i.e. non-catalytic pyrolysis:* 38.9 wt.% organic bio-oil with 38.7 wt.% O_2; *ZSM-5 based catalyst:* 20.7 wt.% organic bio-oil with 30.9 wt.% O_2; *selected natural MgO catalysts:* 25.7 wt.% organic bio-oil with 31.0 wt.% O_2 or 21.1 wt.% organic bio-oil with 28.4 wt.% O_2). The basic sites of the MgO catalysts favored reduction of acids and deoxygenation *via* ketonization and aldol condensation reactions, as indicated by the product distribution and the composition of the bio-oil. Oxygen was removed mainly *via* the preferred pathway of CO_2 formation, compared to CO and water as in the case of ZSM-5 zeolite. On the other hand, reaction coke slightly increased over the MgO catalysts as compared to ZSM-5; however, the MgO formed coke was oxidized/burnt at significantly lower temperatures compared to that of ZSM-5, thus enabling MgO regeneration by relatively mild calcination in air. A systematic correlation of product yields and oxygen content of bio-oil with the physicochemical properties of the MgO catalysts has been established.

1. Introduction

The increase in world energy demand, environmental concerns and the shortage of fossil fuels have driven interest in alternative energy sources. Lignocellulosic biomass is such an alternative and renewable energy source that is abundant, cheap and can be directly converted into liquid, solid and gaseous fuels [1]. A sus-tainable, cost effective utilization of lignocellulosic biomass can diversify the energy balance and reduce the dependence on fossil fuels, leading to a more secure energy supply. Biomass has the added benefit of being compatible with current energy production technologies while it can be also converted to a wide range of commodity chemicals [2–4]. Furthermore, valorization of agricultural wastes, energy crops and forestry by-products, especially *via* decentralized small-size processing units, can offer additional support to the local rural economy.

Lignocellulosic biomass can be converted into liquid, solid and gaseous products *via* the fast pyrolysis process [5–8]. The liquid product (pyrolysis oil or bio-oil) yield can reach up to

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75 wt.% on biomass, depending on the process conditions and the biomass feedstock. The bio-oil is a complex mixture of oxygenated compounds (*i.e.* ketones, phenolics, furans, acids, aldehydes, etc.) derived from the thermal degradation of the holocellulose and lignin fractions in the biomass [9]. Due to its composition, the bio-oil exhibits low calorific value, high viscosity, corrosivity to common metals, immiscibility with hydrocarbon fuels and instability under storage and transportation conditions [9]. It is therefore a low quality product that needs to be upgraded before it can be introduced into the market.

One approach for the production of an upgraded bio-oil is the catalytic fast pyrolysis of biomass, which takes place under the same conditions as thermal fast pyrolysis, with the difference being that pyrolysis vapors come in contact with a solid catalyst prior to their condensation. The catalytic reactions that take place on the catalyst's surface enhance the removal of oxygen in the form of CO_2, CO and H_2O, thus leading to the formation of a bio-oil with tailored composition and improved properties. Furthermore, a de-oxygenated bio-oil can serve as bio-crude and can be treated down-stream, in admixtures with petroleum fractions (*i.e.* gas-oil) in classical (hydro)cracking refinery processes for the production of gasoline and diesel [10]. A wide variety of materials has been suggested as candidate catalysts for the process. Mainly acid catalysts have been studied, such as microporous zeolites, mesoporous aluminosilicates and metal-modified zeolites, while basic catalysts have also been scarcely considered [11]. Naturally-derived activated serpentine and olivine catalysts have been recently investigated for the production of bio-oil with reduced oxygen content [12].

Acid catalysts favor dehydration, decarbonylation, cracking and aromatization reactions [11,13–20]. Aromatization reactions that are favored by the presence of strong zeolitic acid sites lead to the formation of highly valuable monocyclic aromatic hydrocarbons, BTX (*i.e.* benzene, toluene, xylene). However, aromatization reactions are hard to control and contribute also to the formation of polycyclic aromatic hydrocarbons (PAH), which are undesirable due to their known carcinogenic and mutagenic potential. Additionally, PAH can act as precursors of catalytic coke, leading to catalyst deactivation and loss of biomass carbon towards solid products rather than its transformation into desirable liquid products [21]. Among the various acid catalysts, ZSM-5 zeolite is the most frequently studied, as it increases the yield of monocyclic aromatic hydrocarbons and suppresses coke formation due to its unique micropore structure and relatively strong Brönsted acidity [22].

In a previous study [14], we carried out screening of various acidic and basic catalysts for the *in situ* catalytic upgrading of biomass pyrolysis vapors in a fixed bed reactor. The results indicated different bio-oil deoxygenation pathways between the basic and acidic materials. Specifically, the basic catalysts induced high CO_2 yields and bio-oil with decreased acid concentration and high content of ketones, mainly cyclopentanones and cyclopentenones. Ketonization of acids, with simultaneous formation of CO_2, and aldol condensation of aldehydes and smaller ketones were suggested as the prevalent reactions taking place [23,24]. On the other hand, the use of acid zeolitic catalysts (*i.e.* ZSM-5) led to aromatic bio-oils, as mentioned above, with reduced content of oxygenated compounds, while CO and H_2O were the dominant by-products. In terms of carbon efficiency, it would be more desirable to remove oxygen from biomass *via* CO_2 (two O atoms for one C atom) than *via* CO or H_2O. Thus, the use of basic catalysts may open new paths in biomass fast pyrolysis, with regard to the carbon efficiency of the process, the composition of the produced bio-oil and its downstream upgrading. To this end, one of the most attractive candidates as basic catalyst for biomass pyrolysis would be magnesium oxide (MgO). Going further in line with the green chemistry principles,

the use of natural MgO, *i.e.* derived by the calcination of mineral magnesite, could offer a promising cost-effective alternative to the classical synthetic industrial zeolites and related acid catalysts. Catalyst cost is one of the most crucial parameters of catalytic biomass pyrolysis with regard to the economics of the process [25]. The expected tolerance of basic oxide catalysts to deactivation induced by the biomass alkali metals and related ash (*i.e.* Na, K, Ca, Si, etc.) in contrast to the acidic zeolites, is an additional benefit in terms of profitability and economics.

Natural magnesium oxide is produced industrially by thermal decomposition of magnesium carbonate mineral ($MgCO_3$ or magnesite). Natural magnesia can be categorized into two main types, namely caustic-calcined magnesia (CCM, *i.e.* chemically reactive porous magnesium oxide with small crystal size) and dead-burnt magnesia (DBM, *i.e.* non-porous magnesium oxide with high crystal size and very low reactivity), depending on the severity of the thermal treatment of the raw material. Careful beneficiation (process in the mining industry for removing undesirable mineral mixtures form an ore to produce a higher grade product) and calcination of magnesite, leads to CCMs with tuned chemical composition and crystal/particle morphology, thus substantially increasing their added value and broadening their application range to include, among others, the production of catalysts and catalyst supports, a market otherwise typically served by synthetic CCM. Synthetic MgO is usually derived by calcination of $Mg(OH)_2$.

In this work, we investigated the *in situ* upgrading of biomass pyrolysis vapors over various naturally derived basic MgO catalysts. The upgrading potential of these catalysts was compared to that of an industrial ZSM-5 based catalyst formulation, as well as to synthetic MgO materials. Differences in reaction mechanisms and bio-oil composition induced by the basic MgO catalysts compared to acid zeolites were thoroughly discussed.

2. Experimental

2.1. Materials and catalyst preparation

In total, 17 MgO catalysts were investigated (Table 1). These included one natural olivine and 14 natural MgO catalysts prepared either industrially (beneficiation and rotary kiln calcination) or in the laboratory from the calcination of two raw magnesite samples of different purity, *i.e.* Raw-1 (high purity) and Raw-2 (low purity). Depending on the content of impurities (mainly SiO_2 and CaO), the various calcined MgOs listed in Table 1, were characterized as of high purity (SiO_2 and CaO up to 2 wt.%), medium purity (SiO_2 2–7 wt.% and CaO up to 2.5 wt.%), and low purity (SiO_2 25–31 wt.% and CaO 2.9-3.8 wt.%). All natural MgO and olivine samples originated from Grecian Magnesite's Yerakini mine in Northern Greece. In addition, two synthetic industrial caustic calcined magnesia samples were also studied. More information about the various MgO samples are given below.

2.1.1. Laboratory caustic calcined magnesia (CCM) samples

For the laboratory CCM samples (LabCCM-1 to LabCCM-7), the two raw magnesite samples (Raw-1 and Raw-2) were crushed in a laboratory jaw crusher to ±5 mm. An amount of 350 g was then placed on a ceramic plate and calcined in a 1.5 kW laboratory furnace at various temperatures (700–1150 °C) and residence times (60–240 min) to produce MgO samples of varying crystal size, chemical composition and specific surface area (Tables 1 and 2). Ramp-up times to the desired temperature were between 1–3 h, depending on the desired end temperature. After calcination, the samples were milled to ±200 μm in a laboratory disk mill and the 90–200 μm fraction was separated with vibrating sieves.