Catalytic CO₂ hydrogenation using mesoporous bimetallic spinel oxides as active heterogeneous base catalysts with long lifetime

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1. Introduction

CO₂ is a greenhouse gas that significantly contributes to global warming, and hence the concentration of CO₂ exhausted into the atmosphere should be reduced or CO₂ should be removed using various technologies, including capture, sequestration, and utilization [1–4]. Energetically, CO₂ is a very stable low-reactive gas molecule that features two double bonds between its atoms; the activation of its strong double bonds would require significant energy input [5–8]. The addition of an active catalyst to the reaction system is an effective solution for the efficient activation of CO₂, as the catalyst would decrease the activation energy and could ultimately reduce the energy input required for the reaction. The Lewis acid behavior of CO₂ can be explained using the molecular orbital theory, as the energy level of the antibonding molecular orbitals of CO₂ molecules in ground state is high [6–8]. These unoccupied orbitals could act as Lewis acid sites, which could accept external electrons and further activate them. However, the bandgap between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of CO₂ was calculated to be ~10 eV (~964.8 kJ mol⁻¹) [9–11]. Therefore, strongly basic catalysts that exhibit good affinity for the unoccupied orbitals of the CO₂ molecule are required to activate the stable and acidic CO₂ molecule by overcoming such a large bandgap [8,11,12].

The catalytic reduction of CO₂ using H₂ under high pressure is a promising process for the activation of CO₂ [13–15]. One of the main advantages of this approach is the use of reactive H₂ molecules for activating the energetically stable CO₂ molecule in the presence of a catalyst capable of activating both CO₂ and H₂. Numerous studies have been performed in this area during the past several decades. Researchers have used various basic substances not only as catalyst supports to activate H₂, but also as catalysts for the activation of the Lewis acidic CO₂ molecule [16–18]. Typically, basic metal oxide materials that exhibit high porosity and high surface area, which allow them to achieve good dispersion of catalytic metal components, have been used for this purpose. Fe-based catalysts supported on various metal oxides promoted with alkaline metal cations have been investigated for the hydrogenation of CO₂ to hydrocarbons of high molecular weight (usually > C₅). Owing to the fast kinetics of the reverse water-gas shift
were involved in the activation of CO₂, but only the strongly basic sites of their commercial counterparts, which featured lower surface area and adsorption of H₂ would be decreased. This could suppress the formation of CH₄ and eventually increase the selectivity for hydrocarbons of high molecular weight. Surface doping of metal oxide supports with Na or K as promoters could increase the chemisorption of CO₂, whereas the adsorption of H₂ would be decreased. This bifunctional catalyst consisting of reducible In₂O₃ and HZSM-5 zeolite has been investigated for the production of gasoline-range hydrocarbons with almost 80% selectivity, in which it was demonstrated that the oxygen-vacancy sites on the In₂O₃ catalyst could activate CO₂ and H₂ simultaneously.

To convert CO₂ to hydrocarbons of high molecular weight using CO as intermediate, the basicity of the catalyst should be controlled to achieve efficient activation of Lewis acidic CO₂ and adequate adsorption affinity for H₂. The facile and highly selective conversion of CO₂ to CO is the first reaction stage, which should be followed by a FT-type reaction to produce hydrocarbons of high molecular weight. The catalysts used for the FT reaction have been studied more in depth than those used for the CO₂ conversion process and are already commercialized and used in many industries. Therefore, to design such direct and consecutive conversion technology of CO₂ to hydrocarbons of high molecular weight, the development of active catalysts for the first reaction stage of CO₂ to CO should be a priority research topic. Supporting materials, which are usually porous metal oxides, are very important for achieving good catalytic performance as they ensure the proper dispersion of the metal nanoparticles on the catalyst surface. In addition, the adsorption affinity of these materials for CO₂ and H₂ should be delicately controlled for energy-efficient hydrogenation to hydrocarbons of high molecular weight via CO as intermediate. Otherwise, as previously reported, the formation of CH₄ would dominate, which is undesirable for the production of hydrocarbons of high molecular weight.

Although the consensus that the basicity of catalyst support is important has been reached, the catalytic role of supporting materials on the activation of CO₂ during hydrogenation has not been entirely elucidated yet. Therefore, the main goal of this study was to clarify the role of the basicity of metal oxides during the catalytic process as well as their role of support for metal nanoparticles. Therefore, we selected a series of bimetallic oxide materials with spinel structure as catalyst candidates. The unit cell formula of bimetallic spinel oxides is AB₂O₄, where A and B are divalent and trivalent metal cations, respectively, that are covalently bonded to oxygen atoms and form the spinel framework. A variety of metal cations could be used to obtain the spinel framework, which can be a significant advantage for constructing a set of catalysts with the least number of structural variables.

In this study, a series of aluminum spinel oxides where a divalent metal cation is varied with Mg²⁺, Co²⁺, Cu²⁺, Zn²⁺, and Mn²⁺ was synthesized. These spinel oxides presented very different basicity, and hence their catalytic activity was different. In addition, the synthesized mesoporous spinel oxide catalysts presented higher catalytic activity than their commercial counterparts, which featured lower surface area and smaller pore volume. Furthermore, a reasonable catalysis descriptor was discovered from catalytic reactions that used the series of spinel catalysts of different basicity, which proposed that not all basic sites were involved in the activation of CO₂, but only the strongly basic sites can effectively activate CO₂. Systematic studies of the reactions that used the set of spinel oxides as catalysts could shed light on the future design of highly active heterogeneous catalyst for the activation of CO₂ to hydrocarbons of high molecular weight using hydrogen.

2. Experimental

2.1. Synthesis of spinel oxides

Spinel oxides were synthesized via the co-precipitation method by mixing the metal precursors in isopropyl alcohol. Aluminum isopropoxide (>98%, Sigma Aldrich) was used as Al precursor. Mg(NO₃)₂·6H₂O (99%, Junsei Chemical), Co(NO₃)₂·6H₂O (97%, Daegung Chemicals & Metals), Cu(NO₃)₂·2.5H₂O (98%, Sigma Aldrich), and Zn(NO₃)₂·6H₂O (98%, Daegung Chemicals & Metals) were used as Mg(II), Co(II), Cu(II), and Zn(II) precursors, respectively.

In a typical synthesis procedure for CuAl₂O₄ spinel oxide, 0.06 mol (12.255 g) of aluminum isopropoxide was dissolved in 80 g of isopropyl alcohol in a round-bottomed flask, and the resultant solution was heated on a hot plate under reflux and stirring for 2 h. Then, 10 ml of aqueous solution that contained 0.03 mol (6.977 g) of Cu(NO₃)₂·2.5H₂O was added to the flask dropwise, and the resultant solution was further heated on a hot plate under reflux and stirring for 3 h. After the final solution was cooled to room temperature, it was titrated with an aqueous solution of NH₄OH (25–30%, Daegung Chemicals & Metals) to adjust the pH of the solution to 9.5. The resultant solution was further stirred for 3 h, and the solid precipitate was filtered followed by drying in an oven at 100 °C for 12 h. The dried solid powder was calcined in a furnace at 800 °C for 4 h under O₂ flow (100 cm³ min⁻¹), which led to the formation of crystalline CuAl₂O₄.

The synthesis procedure and gel composition of all other spinel oxides were the same as that described above, only different nitrates were used as metal precursors.

2.2. Characterisation

The X-ray diffraction (XRD) patterns of the synthesized spinel oxides were obtained using a Rigaku MiniFlex 600 apparatus with Cu Ka radiation (λ = 0.1541 nm) at 40 kV and 15 mA (600 W). All measurements were performed under ambient conditions, at the step size of 0.02°, the scanning rate of 2° min⁻¹, and in the 2θ range of 25° to 70°. The X-ray diffraction patterns of the spinel oxides were indexed using the JCPDS database.

The surface area of the spinel oxide samples was calculated using the Brunauer-Emmett-Teller (BET) theory [28], and their total pore volume and pore size distribution were obtained from the adsorption branches using the Barrett-Joyner-Halenda (BJH) algorithm [29]. Transmission electron microscopy (TEM) images were obtained using a Tecnai F-20 (Philips) instrument operating at 200 kV (lattice resolution: 0.19 nm). Images were recorded using a CCD camera at high magnification under low-dose conditions. CO₂ or NH₃ temperature-programmed desorption (TPD) measurements were carried out using a BEL-CAT (BEL Japan, Inc.) analyzer. The exhaust gases desorbed from the spinel oxide samples were analyzed by thermal conductivity detector (TCD), which allowed quantitative and qualitative analyses of basic and acidic sites. Prior to the CO₂-TPD measurement, CO₂-TPD with quadrupole mass spectrometer confirmed that most of desorbed species during CO₂-TPD process was species having m/z = 44 corresponding to CO₂ and traceable amounts of other components such as O₂ with m/z = 32 were observed. Prior to the TPD measurements, all samples were pre-treated using a stream of He for 1 h at 500 °C in a quartz cell followed by cooling to 50 °C. The adsorption of CO₂ and NH₃ was performed using 19.8%CO₂/He and 5% NH₃/He flows, respectively, for 1 h. After purging the cell with He for 30 min, TPD measurements were performed by increasing the temperature of the cell from 50 to 980 °C (ramping rate of 10 °C min⁻¹) and maintaining the temperature at 980 °C for 1 h under He flow.
2.3. Catalytic reaction

The hydrogenation of CO₂ was performed in an Inconel continuous flow fixed-bed microreactor (Scheme S1 in Supporting Information). The reaction was conducted at 20 bar and various temperatures (300, 320, 350 and 400 °C), and the gas flow rates were controlled using a mass flow controller (LineTech). The temperature of the reactor was monitored using a thermocouple located inside the catalyst bed. During a typical reaction, 0.5 g of catalyst was physically mixed with 1.0 g of sea sand (14–20 mesh, Wako Chemicals), and the mixture was placed on a fixed bed inside the microreactor. The catalyst was pretreated by purging it with Ar (50 cm³ min⁻¹) which was followed by the addition of H₂ (60 cm³ min⁻¹) for the reduction reaction while increasing the temperature to 400 °C under ambient pressure conditions (Scheme S2 in Supporting Information). After the temperature reached 300 °C, the gas mixture that contained 21% CO₂, 63% H₂, and 16% balance gas (Ar) (flow rate: 84.0 cm³ min⁻¹) was introduced into the reactor (GHSV = 10 080 cm³ g⁻¹ h⁻¹). After 200 min, the reaction temperature was further increased to 320, 350 and 400 °C consecutively at the ramping rate of 1 °C min⁻¹. The process was monitored for 200 min at each reaction temperature. The reaction was monitored using a gas chromatography (GC) instrument that was connected to the outlet of the reactor. The GC instrument was equipped with a flame ionization detector (FID) connected with a capillary column (HP-INNOWAX, 30 m length, 0.20 mm diameter, 0.50 μm thickness) and a thermal conductivity detector (TCD) connected with a packed column (Supelco Analytical Metal packed GC column, 1.5 m length, 1/8-inch outer diameter, 2.1 mm inner diameter). The carbon balances for all reactions were calculated, and the average values for all reactions were approximately 95%.

3. Results and discussion

3.1. Catalyst characterisation

The crystalline structure of the synthesized spinel oxides was characterized using powder XRD, and was compared with that of a commercially available spinel oxide (i.e., MgAl₂O₄(comm.), Sigma Aldrich). As shown in Fig. 1A, the XRD peaks of all the materials could be assigned to the same Miller indices, which confirmed that the typical XRD patterns corresponded to the crystal structure of spinel. All reflections were located at positions similar to those of MgAl₂O₄(comm.) with similar relative peak intensities. However, a small discrepancy in the peak positions was observed owing to the different lattice parameters that originated from the different sizes of the divalent metals present in the spinel frameworks. The XRD intensities with peak broadness were different and depended on the divalent metal present in the spinel framework. Particularly, the peaks of the synthesized MgAl₂O₄ spinel were broader than those of MgAl₂O₄(comm.), which suggested that the structure of the synthesized spinel was nanocrystalline.

Figs. 1B and C shows the N₂ adsorption isotherms and corresponding pore size distributions, respectively, or the synthesized spinel oxides. All synthesized spinel oxides presented type IV isotherms with hysteresis loops in the high relative pressure (P/P₀) range of 0.4-0.9, which could serve as evidence for their mesoporous structure. A steep increase in the amount of adsorbed N₂ was observed in this relative pressure range, which indicated the adsorption of N₂ inside the mesopores. By contrast, MgAl₂O₄(comm.) adsorbed very small amounts of N₂, and the amount of adsorbed N₂ did not significantly increase in the high P/P₀ range. Therefore, it was concluded that the pore volume and surface area of the MgAl₂O₄(comm.) sample were smaller than that of the synthesized mesoporous MgAl₂O₄. The BET surface area of the synthesized MgAl₂O₄ sample was approximately three times higher than that of the MgAl₂O₄(comm.) (199 vs. 77 m² g⁻¹) while the total pore volume of the synthesized MgAl₂O₄ sample was twice as large as that of the MgAl₂O₄(comm.) (0.47 vs. 0.24 cm³ g⁻¹) (Table 1).

The mesoporous structure of spinel oxides was further characterized using TEM (Fig. 2). All spinel oxides exhibited highly nanocrystalline frameworks, and the individual spinel nanocrystals were different in size. The bright void spaces observed between the nanocrystals corresponded to the intercrystalline mesopores, and their presence was already confirmed using the N₂ adsorption analysis results. Crystal lattice fringes could only be conspicuously observed for ZnAl₂O₄. In addition, the individual ZnAl₂O₄ spinel nanocrystals were slightly larger than those of the other analyzed spinel oxides. This was consistent with the features of the XRD spectra, wherein ZnAl₂O₄ presented the most intense XRD reflections of all spinel oxides in this study.

The basic properties of the spinel oxide samples were analyzed using CO₂ TPD. Fig. 1D depicts the CO₂ TPD profiles of all spinel oxide samples, and includes quantitative and qualitative information on their basicity after the deconvolution of the original TPD profiles depending on the desorption temperature. The TPD profiles of the spinel oxide samples were noticeably different, which indicated that their basic properties were significantly different. The spinel oxide samples presented different amounts of basic sites of different strengths (Table 1). The total amounts of basic sites of CuAl₂O₄, CoAl₂O₄, and MgAl₂O₄ were similar and ranged from 140 to 150 mmol g⁻¹. By contrast, the total amount of basic sites of ZnAl₂O₄ was the smallest (~30 mmol g⁻¹) of all samples. The strength of the basic sites could be determined...
Of all spinel oxide samples, CuAl₂O₄ presented a very intense TPD signal at approximately 980 °C, followed by CoAl₂O₄, which presented an intense peak at approximately 900 °C. The integrated area of the TPD peaks at higher desorption temperature (> 800 °C) was used to estimate the quantity of strong basic sites, and it was determined that the amount of strong basic sites decreased as follows: CuAl₂O₄ > CoAl₂O₄ > MgAl₂O₄(comm.) > ZnAl₂O₄ > MgAl₂O₄.

Namely, the CuAl₂O₄ sample presented the largest amount of basic sites of all analyzed spinel oxide samples. The acidic properties of spinel oxide samples are also analyzed using NH₃ TPD (Fig. S1 and Table S1 in Supporting Information), demonstrating that the acidic properties are also significantly different depending on the spinel oxide samples. However, the absolute amounts of acidic sites of all spinel oxide samples were almost negligible compared with the amounts of basic sites, and therefore, it was concluded that the basic character of the spinel oxide samples was predominant.

The reducibility of spinel oxide samples was measured with H₂ TPR (Fig. S2 in Supporting Information). Of all the spinel oxide samples, MgAl₂O₄(comm.) showed two distinct H₂ consumption peaks at 500 and 750 °C, indicating that the MgAl₂O₄(comm.) is highly reducible. In contrast, it is noteworthy that no intense H₂ consumption peaks were observed in the synthesized MgAl₂O₄ sample, indicating that the mesoporous MgAl₂O₄ synthesized in this work is almost non-reducible. Similarly, ZnAl₂O₄ sample was much more non-reducible without any H₂ consumption peaks, and hence H₂ TPR data for ZnAl₂O₄ sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Textural properties</th>
<th>Amount of basic sites (mmol g⁻¹)</th>
<th>Arrhenius plot results and derived parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S_BET(1) (m² g⁻¹)</td>
<td>D_β(2) (nm) V_(T)(3) cm³ g⁻¹</td>
<td>B_w(4) mmol g⁻¹</td>
</tr>
<tr>
<td>ZnAl₂O₄</td>
<td>50</td>
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<td>0.25</td>
</tr>
<tr>
<td>CuAl₂O₄</td>
<td>44</td>
<td>9.4</td>
<td>0.13</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>156</td>
<td>4.9</td>
<td>0.30</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>199</td>
<td>3.3</td>
<td>0.47</td>
</tr>
<tr>
<td>MgAl₂O₄ (comm.)</td>
<td>77</td>
<td>4.8</td>
<td>0.24</td>
</tr>
</tbody>
</table>

(1) Total surface area calculated using the Brunauer–Emmet–Teller (BET) method.
(2) Average pore diameter calculated using the Barrett–Joyner–Halenda (BJH) method.
(3) Total pore volume calculated using the BJH method.
(4) Amount of weak strength basic sites obtained from the deconvoluted CO₂ TPD profiles in the temperature range of 50-500 °C.
(5) Amount of medium strength basic sites obtained from the deconvoluted CO₂ TPD profiles in the temperature range of 500-800 °C.
(6) Amount of strong basic sites obtained from the deconvoluted CO₂ TPD profiles in the temperature range of 800-980 °C.

Table 1
Characterization results of synthesized spinel oxide catalysts and commercial MgAl₂O₄(comm.) catalyst; Arrhenius plots results and their derived parameters (E_a and A are the activation energy and pre-exponential factor, respectively).

Fig. 2. Transmission electron microscopy images of mesoporous spinel oxide samples: (A) ZnAl₂O₄, (B) CuAl₂O₄, (C) CoAl₂O₄, and (D) MgAl₂O₄. (Scale bar = 20 nm).
could not be acquired. CoAl₂O₄ sample showed a very broad H₂ consumption peak beyond 600 °C. Such high reduction temperature indicated that CoAl₂O₄ sample is also less reducible. In contrast, CuAl₂O₄ sample show a distinct H₂ consumption peak at 210 °C, which might be attributed to the reduction of Cu²⁺ inside the CuAl₂O₄ framework to Cu⁺. All the spinel oxide samples were further characterized with XRD after the reduction at 400 °C under the pretreatment condition using H₂/Ar flow and compared with the fresh samples before the pretreatment (Fig. S3 in Supporting Information). After pretreatment, the initial spinel structure was fully maintained for all the samples, but most of the XRD peaks were broadened. Of all the spinel oxide samples, only CuAl₂O₄ sample showed a distinct H₂ consumption peak below 400 °C. However, any additional XRD peaks were not appeared for the pretreated CuAl₂O₄ sample. This suggested that the quantity of reduced phase was very small. In overall, it could be stated that the pretreatment condition for the following reaction studies could not make any distinguishable metallic phase and the spinel phase could be almost fully maintained due to its very stable and rigid crystalline architecture.

3.2. Hydrogenation of CO₂ using spinel oxide catalysts

The catalytic activity of the spinel oxide samples was investigated during the hydrogenation of CO₂ under pressurized H₂ gas. Fig. 3 illustrates the kinetic reaction profiles of the four synthesized spinel oxide catalysts compared with that of the MgAl₂O₄(comm.) catalyst at the reaction temperatures of 300, 320, 350 and 400 °C as functions of the time-on-stream (Figs. 3A–E), and the respective CO₂ conversion and product selectivity average values at different reaction temperatures (Figs. 3F–J and Table 2). The reaction results demonstrated that the spinel oxide catalysts presented apparent catalytic activity for the hydrogenation of CO₂. Depending on the catalysts and reaction temperature, the average conversion values of CO₂ ranged from ~5% to ~45% (closed black circles in the graphs in Fig. 3). Such high conversion values were remarkable for the reaction conditions in this study, where the GHHSV (10 080 cm³ g⁻¹ h⁻¹) value was high. While most spinel oxide catalysts continuously convert CO₂ without appreciable deactivation during the reaction process (Figs. 3A–E), the CO₂ conversion capacity of CoAl₂O₄ gradually decreased as the reaction went on. When CoAl₂O₄ was used as catalyst, CH₄ was the major reaction product, and its selectivity was approximately 80% at the tested reaction temperatures. By contrast, the other spinel oxide catalysts were more active for generating CO as the major product, and their selectivity exceeded 78% at all reaction temperatures, of which the reaction may follow the RWGS reaction pathway. Small amounts of CH₄ and CH₃OH were also produced as minor products, but their selectivity did not exceed ~20% upon increasing the reaction temperature to 400 °C.

The distinct deactivation phenomenon observed for the CoAl₂O₄ catalyst could be explained by the formation of CH₄ as the major product. Compared with other spinel oxide catalysts, CoAl₂O₄ produced more than 80% CH₄ as the major product. Co-based materials are very effective catalyst for the CO₂ methanation as well as the production of CH₄ via FT-type syngas (CO + H₂) conversion [24,30–32]. Similar to the Co-based catalysts reported in other papers, the CoAl₂O₄ catalyst in this study was also very active for the formation of CH₄ [21,33,34]. When CH₄ is produced during the hydrogenation of CO₂, metal carbide species could form on the surface of the catalyst, and these carbide species could react with H₂ to generate reactive CH₄ species that could be further hydrogenated to CH₄. During this process, the main catalytic sites could be gradually deactivated owing to the formation of metal carbides [30,35]. Similarly, the deactivation of the CoAl₂O₄ catalyst in our study could be attributed to the formation of cobalt carbide (Co₂C) species on the surface of the catalyst. When the XRD spectra of the spent and fresh CoAl₂O₄ catalyst samples were compared, it was possible to identify the cobalt carbide (Co₂C) phase at 2θ value of 42.5° (Fig. S4 in Supporting Information) [36]. In addition, a thin layer of carbonaceous structure with ca. 1.1 nm thickness was observed on the external surface of spent CoAl₂O₄ catalyst (Fig. S5 in Supporting Information).

Of all spinel oxide catalysts in this study, only CoAl₂O₄ presented appreciable deactivation. Moreover, the major reaction product of all spinel oxide catalysts, except for CoAl₂O₄, was CO, and their selectivity exceeded 78%. When CO was the major product, no reactive carbonaceous species and CH₄ species could be formed during the conversion of CO₂ to CO. Accordingly, the surface of the catalyst remained almost intact during the reaction process, and no significant deactivation occurred. In addition, almost no differences were observed in the XRD
patterns and peak intensities of the spent and fresh spinel oxide catalysts, except for CoAl2O4 (Fig. S4 in Supporting Information).

The catalytic activity of all spinel oxide catalysts depended on the reaction temperature. CuAl2O4 exhibited the highest CO2 conversion (average value of 25.8%) at low reaction temperature (300 °C), and the conversion degree significantly decreased as follows: CoAl2O4 (16.5%) > ZnAl2O4 (7.0%) > MgAl2O4 (5.1%) > MgAl2O4(comm.) (4.8%). The CO2 conversion values of all spinel oxide catalysts increased as the reaction temperature increased. At 400 °C, CoAl2O4 presented the strongest catalytic activity and the conversion of 45.7%, followed, in order, by CuAl2O4, ZnAl2O4, MgAl2O4, and MgAl2O4(comm.). However, except for the CuAl2O4 catalyst, which generated CH4 as the major reaction product, CuAl2O4 exhibited the highest catalytic activity of all spinel catalysts that generated CO as the major reaction product, and its average CO2 conversion value was 38.6% at 400 °C. Therefore, CuAl2O4 was the most active catalyst for the conversion of CO2 to CO at the tested reaction temperatures. It is noteworthy that CuAl2O4 spinel oxide catalyst maintained its initial catalytic performances up to four repetitive reaction tests without significant deactivation and changes in product selectivity (Fig. S6 and Table S2 in Supporting Information).

### 3.3. Effect of basicity of spinel catalysts during hydrogenation of CO2

We attempted to correlate the catalytic activity of all spinel oxide catalysts with their properties. According to the CO2 and NH3 TPD analysis results, the basicity of all spinel oxide catalysts was high and their acidity low. Typically, the Lewis acidic CO2 molecule should be adsorbed on basic sites for its activation, and consequently, the amount of CO2 converted during a given reaction time would be correlated with the number of basic sites of each spinel oxide catalyst. When the average CO2 conversion values were plotted against the total quantity of basic sites, the graphs consisted of very scattered data points and no systematic relationships were observed (Fig. S7 in Supporting Information). This could suggest that only a fraction of all basic sites were directly involved in the activation of CO2. However, when the CO2 conversion was plotted against the quantity of strong basic sites determined using the CO2 TPD results, a linear relationship was observed (Fig. 4). As the amount of strong basic sites of the spinel oxide catalysts increased, the CO2 conversion increased linearly. The correlation coefficient (R2) was almost 1 at the low reaction temperature of 300 °C, but significantly deviated from 1 as the reaction temperature increased to 400 °C. However, the linear relationship between the amount of strong basic sites and the CO2 conversion could still be observed at the tested reaction temperatures.

From the above findings that the strong basic sites were directly involved in the activation of CO2 during the hydrogenation reaction, it was proposed that the amount of strong basic sites of spinel oxide catalysts could be the catalysis descriptor that would explain the activation of CO2. In addition, the strong basic sites could be considered the actual catalytic sites for the activation of CO2. Based on this assumption, the thermodynamic parameters of the reaction could be obtained using the Arrhenius equation at four different reaction temperatures. Fig. 5 depicts the Arrhenius plots: the turnover frequency (ln(TON), s⁻¹) as function of temperature (1000/T, K⁻¹), of the reactions that used the synthesized and commercially available spinel oxides as catalysts. The TOF was calculated using the amount of CO2 converted on the strong basic sites of all spinel oxide catalysts during a given reaction time. The activation energies (Ea) and pre-exponential factors (A) could be derived from the y-intercept and slope of the linear regression, respectively, of these linear plots. All plots presented linear regression, and the R2 values were very close to 1. The Ea values of CuAl2O4, MgAl2O4(comm.), MgAl2O4, CoAl2O4, and ZnAl2O4 increased from 13.0 to 14.6, 17.1, 30.9, and 39.7 kJ mol⁻¹, respectively. The contribution of CuAl2O4 to the reduction of the activation energy was the greatest of all studied catalysts, which indicated that its catalytic power for activating the RWGS reaction was the strongest of all analyzed catalysts at the tested reaction temperatures. In addition, the Ea value of the CuAl2O4 catalyst for the RWGS reaction was much smaller than those reported in the literature for Cu-based heterogeneous catalysts [37–39]. The Ea value of the Cu/ZnO catalyst, which was obtained using ZnO as support for metallic Cu, for the RWGS reaction, exceeded 50 kJ mol⁻¹ [37–39]. This was attributed to the strong basicity of CuAl2O4 compared with those of other Cu-based heterogeneous

### Table 2

Summary of reaction results for CO, CH4, and CH3OH obtained from Figs. 3F–3J for all tested spinel oxide catalysts.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>ZnAl2O4</th>
<th>CuAl2O4</th>
<th>CoAl2O4</th>
<th>MgAl2O4</th>
<th>MgAl2O4 (comm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>320</td>
<td>350</td>
<td>400</td>
<td>300</td>
<td>320</td>
</tr>
<tr>
<td>CO2 conv. (%)</td>
<td>7.0</td>
<td>9.0</td>
<td>14.1</td>
<td>23.7</td>
<td>25.8</td>
</tr>
<tr>
<td>Sel. (%)</td>
<td>90.6</td>
<td>89.8</td>
<td>81.8</td>
<td>96.8</td>
<td>94.3</td>
</tr>
<tr>
<td>CH4 (%)</td>
<td>1.7</td>
<td>2.4</td>
<td>5.1</td>
<td>12.7</td>
<td>80.4</td>
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<tr>
<td>CH3OH (%)</td>
<td>1.8</td>
<td>1.3</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
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</table>

Fig. 4. CO2 conversion (%) vs. quantity of strong basic sites (mmol g⁻¹) of synthesized spinel oxide catalysts and commercial MgAl2O4(comm.) catalyst at (A) 300, (B) 320, (C) 350 and (D) 400 °C.
catalysts, which could bind CO2 very strongly for its activation. As proposed above, the strong basic sites could be the catalytic sites for activation of CO2. The strong basic sites might be related with the oxygen-vacancy sites in the spinel framework, at which the CO2 molecules could be bound via strong chemisorption. Recently, it was reported that the oxygen-vacancy sites in In2O3 catalyst could be the catalytic sites for CO2 hydrogenation in the presence of H2 [27]. According to this work, CO2 molecules could annihilate the oxygen-vacancy sites via strong adsorption. Such oxygen-vacancy sites were also active for H2 activation, and thus the CO2 molecules could be hydrogenated into hydrocarbons via CO as the intermediate species. Similarly, in the present work, the strong basic sites might be the oxygen-vacancy sites having the strong adsorption affinity to CO2 molecules, which could be the catalytic sites for activation of CO2. If this is the case, H2 molecules could also be activated by the oxygen-vacancy sites though the distinguishable metallic phases were not present. Consequently, CO2 and H2 molecules could be simultaneously activated on the strong basic sites (i.e., oxygen-vacancy sites), as reported above [27].

The pre-exponential factor (A) is a mathematical constant, but it can provide physical information about the collision frequency. The collision frequency of mesoporous MgAl2O4 was one order of magnitude higher than that of MgAl2O4(comm.). This could be explained by the highly mesoporous structure allowing for more facile molecular diffusion, which increased the collisions of CO2 with the surface of the catalyst. Therefore, the mesoporous structure significantly contributed to the higher catalytic activity of MgAl2O4 compared with that of MgAl2O4(comm.). In addition, the mesopore void spaces could be further used to support and disperse additional catalytic metal components. This will be investigated in more details in future studies.

4. Conclusions

Mesoporous bimetallic spinel oxides were synthesized using the co-precipitation of divalent and trivalent metal components under basic conditions. Depending on the divalent metal (Mg, Co, Cu, and Zn) present in the spinel framework, the resultant spinel oxides exhibited different porosity (surface area, pore volume, and pore size) and basicity (quantity and strength of basic sites). Owing to their strong basic sites, which could adsorb Lewis acidic CO2, all spinel oxides exhibited sufficiently high catalytic activity during the conversion of CO2 under hydrogenation conditions even in the absence of additional catalytic metal components for the activation of H2. The catalytic activity of the spinel oxides was high, and their average CO2 conversion values ranged from ∼5% to ∼45% depending on the reaction temperature (300, 320, 350 and 400 °C). The major contribution of this study was the discovery of a catalysis descriptor that linearly correlated with the catalytic activity of the spinel oxides: not all basic sites contributed to the activation of CO2, only the sufficiently strong ones did. Of all spinel oxide catalysts analyzed, CuAl2O4 possessed the largest amount of strong basic sites, and hence, it exhibited the strongest catalytic power and featured the smallest Ea value for the activation of CO2 to produce CO via the RWGS reaction pathway. The spinel oxide catalysts synthesized in this study are under further investigation for designing multifunctional catalysts having additional catalytic metal nanoparticles. Such catalysts could present tandem catalytic functions that could facilitate the conversion of CO2 to CO, which could subsequently be converted to hydrocarbons of large molecular weight via the FT-type reaction pathway.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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