The catalytic decomposition of carbon dioxide on zinc-exchanged Y-zeolite at low temperatures

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Abstract

Background: We report our recent study on the use of a zinc-modified NaY zeolite to decompose CO2 at the temperature range between 300 °C and 550 °C.

Results: At a reaction temperature of 450 °C we observed that 70% of CO2 was converted with an insignificant quantity of CO produced. Scanning electron microscopy and Fourier transform infrared spectroscopic analysis of the neat and spent catalysts confirmed the presence of carbon nanostructures after the reaction. In addition to this CHN analysis support these results by providing weight percent (0.73 wt%) of carbon after reaction. Stability of the catalyst was further confirmed with slight/no change in x-ray diffraction technique.

Conclusion: This route potentially offers a facile strategy to achieve CO2 decomposition and an explanation on the formation of carbon on zinc-modified zeolite catalysts.

Keywords: Catalytic decomposition of CO2, zinc-modified NaY zeolite, catalyst activation.
1. Introduction

The increasing concentration of carbon dioxide (CO₂) in the atmosphere is considered as one of the major factors that contributes to climate change. In order to reduce the anthropogenic carbon emissions from various industrial activities, CO₂ can be separated from industry effluent streams to prevent its entry to the atmosphere. Sorption-based CO₂ separation processes are effective. However, they are generally energy intensive processes and are optimised towards large scale operations. There are conversion approaches whereby CO₂ is catalytically converted into value-added products such as methanol and gasoline. This conversion strategy presents an attractive pathway to utilise CO₂. The idea of decomposing CO₂ into carbon and oxygen via a thermal process has been proposed (1). However, the high stability of CO₂ molecule requires the reaction to be operating at temperatures between 3,200 K and 4,600 K (2). The energy intensiveness of this reaction renders this reaction to be a net producer of CO₂. The use of catalyst to reduce the activation requirement have been attempted. Tamura et al. (3) first reported the complete reduction of carbon dioxide by using cation excess magnetite at 563 K. They showed that by increasing the cation concentration in the magnetite structure under a reductive environment at elevated temperatures, the reduced magnetite could break the carbon-oxygen bond by abstracting an oxygen atom from the CO₂ molecules. Kodama et al., Zhang et al., Wada et al. (4-6) also showed that different forms of ferrites and magnetite could be used to decompose CO₂ at higher efficiencies. A common finding from all these studies is that the activity of catalysts was strongly dependent on the degree of reduction of the oxide materials, which was found to be controlled by the amount of oxygen deficient sites in the catalyst.

Different types of metal-based catalysts, in particular iron-based oxides, have been tested with the aim to improve the rate of CO₂ decomposition. The overall reaction mechanism of CO₂ decomposition by ferrites-based catalyst can be generally described by Equations (1) and (2) (7),

\[
MF_{e2}O_4(s) + \delta H_2(g) \rightarrow MF_{e2}O_{4-\delta}(s) + \delta H_2O(g) \tag{1}
\]

\[
MF_{e2}O_{4-\delta}(s) + CO_2(g) \rightarrow MF_{e2}O_4(s) + CO_{2-\delta}(g) \tag{2}
\]
where M represents the second metal in these ferrite structures. Nickel ferrite, chromium-doped nickel ferrite, nickel-zinc \((\text{Ni, Zn})\) ferrite, nickel-copper-zinc \((\text{Ni, Cu, Zn})\) ferrite, cobalt ferrite, copper ferrite and manganese ferrite \((8-17)\), were found to be catalytically active for the complete decomposition of \(\text{CO}_2\). Lin et al., Ma et al. and Kim et al. studied the activity of nickel ferrite and zinc ferrite for carbon dioxide decomposition \((8, 9, 11)\). In these studies, nickel ferrite was found to be highly active towards carbon dioxide decomposition at temperatures as low as 300 °C. Most importantly, the size of the doped particles as well as oxygen deficiency were found to significantly affect the activity of the catalyst. However, in all cases, the coke formed upon carbon dioxide decomposition led to the deactivation of catalysts. Because of this, the effect of binary as well as ternary metal doping for carbon dioxide decomposition was also studied by Ma et al., Farghali et al. and Khedr et al. \((13-15)\). These metal oxides include copper, nickel as well as zinc ferrite. It was reported that the interfacial chemical reactions and the solid-state diffusion are the two rate-determining steps in the overall process which involved copper ferrite. In addition, doping copper ferrite with nickel helped to reduce the decomposition temperature of \(\text{CO}_2\). Along with the doping, the effect of size of particles was also studied which shows that smaller particles size results in single walled carbon nanotubes whereas larger particles resulted in multiwalled carbon nanotubes. Although the presence of zinc in the catalyst was found to provide higher thermal stability to these catalysts at higher operating temperatures \((11)\), rapid deactivation, relatively long reaction times and low yields of carbon have limited the applications of these catalysts.

Wang et al. studied the decomposition of \(\text{CO}_2\) at 300 °C by using zinc-modified Y zeolite (Zn-Y) and showed that the presence of higher contents of Lewis acid sites in zinc-impregnated zeolite and the delocalized electrons in the vicinity of framework were responsible for the decomposition of \(\text{CO}_2\) though the overall activity of \(\text{CO}_2\) decomposition was found to be very low \((2)\). Nevertheless, this study opened the possibility of activating and converting carbon dioxide under relatively mild conditions. The present study aims to (i) develop zinc-modified zeolite materials by adopting facile methods of synthesis and activation, and (ii) demonstrate the catalytic activities of these material when used for \(\text{CO}_2\) decomposition.

2. Experimental

2.1 Catalysts preparation
Zinc acetate and NaY zeolite were purchased from Sigma-Aldrich and used without further purification. Zinc-modified NaY zeolite was synthesized by the ion exchange method, which is a reliable technique to produce consistent catalyst structures for different applications. In brief, the pre-determined amount of zinc acetate was dissolved in deionized water to form a 1.0 M solution followed by the addition 1 g of NaY zeolite. This slurry was continuously stirred for 15 hours at 60 °C before the solid was recovered by filtration. The filtered solid was washed with low conductivity water and then dried in the oven at 100 °C. The aforementioned ion-exchange, washing and drying procedure was repeated three times to ensure that all the available sites in NaY zeolite were exchanged as well as to maintain batch-to-batch reproducibility. The washing and drying procedure also ensured that any unbound zinc entity is removed from the zeolite structure. This ion exchange method founds to be beneficial for the formation of high ratio of Zn-O-Zn bridging species inside the channel of the zeolite as well as more Lewis acidic sites which further create impact on catalyst performance(18).

2.2 Characterization of catalysts

The crystallinity and structure of the catalysts were examined by using Bruker AXS D8 Advance wide-angle X-ray diffractometer, 2400 II CHNS/O Elemental analyser- PerkinElmer for elemental analysis of carbon, Fourier transform infrared (FTIR) spectra of catalysts were recorded using a Perkin-Elmer Frontier MID/FAR IR instrument with a diamond attenuated total reflectance (ATR) accessory. Scanning electron microscopy (SEM) and Energy Dispersive X-Ray (EDX) Spectroscopy were performed by using FEI Nova NanoSEM 200 FEGSEM. In order to quantitate the amounts of zinc loaded to the catalyst samples, a predetermined amount of each sample was digested in aqua-regia. The amount of dissolved zinc in the supernatant was analysed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and the results obtained were used to determine the zinc content in fresh and used catalyst samples.

2.3 Catalytic reactor setup and catalyst screening.

The decomposition of CO₂ was studied over different zeolite catalysts in a tubular batch reactor. Unexchanged NaY zeolite was also used as a control to study the role of zinc in CO₂ decomposition reaction. High purity gases including Ar, 5% H₂ (balanced in Ar) and 10% CO₂
(balanced in Ar) were used in the gas phase experiments. In a typical experiment, 1.0 g of catalyst was packed in the stainless-steel tubular reactor (ID= 0.7 cm and H= 64 cm) which was then placed vertically inside an electrical split furnace. Under such circumstances, the catalyst bed occupied a volume of 0.50 mL. The two-step pre-treatment of the catalyst was found to be a critical step in the CO₂ decomposition reaction in this study. Initially the temperature was increased to 120 °C and maintained at this temperature for an hour before it was further increased to 350 °C. In this procedure, a slow heating rate of 1-2 °C/min was adopted to minimise thermal shock to the materials and to avoid the development of a huge temperature gradient. This helped to eliminate pore damage by rapidly expanded water vapour. Subsequently, the catalyst was activated by flowing 5% H₂ in argon at 700 °C for 3 hours. The reduction of the catalyst by using H₂ gas results in the generation of the Zn metallic sites in the catalyst which found to be active towards decomposition reaction. Finally, the catalyst bed was cooled to room temperature slowly at a cooling rate of 5 °C/min under a constant flow of argon gas. During this step, any unabsorbed or loosely adsorbed H₂ molecules were removed from the catalyst surface. Once the pre-treatment procedure was completed, the catalyst was said to be in its activated state and was ready to be used for CO₂ decomposition. In a typical catalyst testing experiment, a gas stream containing 10% CO₂ in argon was allowed to flow (20 mL/min) through the tubular reactor at room temperature until a steady concentration of CO₂ was established in the system. Then the reactor was isolated by using the isolation valves that were connected to the top and at the bottom end of the reactor. The decomposition of CO₂ was studied in temperature range of 275 -500 °C. After 1 hour of reaction at given temperature, the gas content inside the reactor was transferred to the online GC for compositional analysis. Gas compositional analysis was performed by using PerkinElmer Clarus 500 Gas Chromatograph (GC) equipped with a thermal conductivity detector (TCD) with molecular sieve column (HayeSep Q and Molecular Sieve).

3. Results and discussion

Table 1 shows the measured CO₂ conversion and the formation of CO at different reaction temperatures. Carbon monoxide was one of the reaction products that could be formed from the Boudouard reaction in the presence of CO₂ and carbon (Equation 3).

\[ 2CO_{(g)} \leftrightarrow CO_{2(g)} + C_{(s)} \] (3)
The catalysts used for CO$_2$ decomposition were neat NaY zeolite (control) and Zn-NaY zeolite. When NaY zeolite was used for the reaction, the concentration of the CO$_2$ remained unchanged for reaction temperatures below 275 $^\circ$C. The lack of activity suggests that NaY was not active below this temperature threshold. As the reaction temperature was increased to 300 $^\circ$C a small (1.4%) yet detectable conversion of CO$_2$ was observed. Under this condition, no gas other than CO$_2$ was detected in the system. The conversion of CO$_2$ continued to increase with increasing reaction temperature and reached up to 20% at 450 $^\circ$C. However, a significant amount of CO started to form when the reaction temperature was increased to 400 $^\circ$C. At this temperature, it appeared that sufficient energy was provided to convert the CO$_2$ into CO, and that the CO produced was not adsorbed by the catalyst structure and emerged in the gas phase. The detection of the CO gas by the detector provides an evidence that the formed CO does not adsorbed on the zeolite structure. In addition, the temperature of the reaction itself comes in the range of CO desorption region on the catalyst. Carbon monoxide was the only product detected during reaction when NaY was used.

Table 1 also provides the CO$_2$ conversion data when Zn-NaY zeolite catalyst was used at different reaction temperatures. The onset reaction temperature when Zn-NaY zeolite showed detectable CO$_2$ decomposition activity was 275 $^\circ$C. As the reaction temperature was increased to 300 $^\circ$C a CO$_2$ conversion of 16.1% was recorded. As the reaction temperature was increased further to 450 $^\circ$C the conversion of CO$_2$ was found to be four times higher. More importantly, the decrease in CO$_2$ concentration was not accompanied by any CO or CH$_4$ formation which suggested that CO$_2$ was directly decomposed into carbon and oxygen by the catalyst. It was also found that over the reaction temperature range of 275 $^\circ$C to 550 $^\circ$C the CO$_2$ conversion peaked at 450 $^\circ$C and gradually decreased to a lower value at 550 $^\circ$C. In additional, noticeable amounts of CO were apparent between 450 $^\circ$C and 550 $^\circ$C which suggested that CO was likely to be formed from the carbon generated from CO$_2$ decomposition on the catalyst surface via the Boudouard reaction. The presence of carbon deposits was also responsible for the decrease in the available surface sites for CO$_2$ decomposition. In addition to this, there was a ~70% reduction in the CO$_2$ concentration at 450 $^\circ$C and less than 1% CO formation with almost 3.7% of oxygen formation along with 0.73wt% of carbon determined via elemental analyser. However, results from digestion analysis confirmed that there were small yet noticeable decreases in zinc content after hydrogen reduction. For example, based on the control
experiment, the amount of zinc before hydrogen reduction was 85.6±5.0 mg/g of catalyst and this value decreased to 76.3±5.0 mg/g after hydrogen reduction. This decrement was attributed to the formation of volatile zinc under hydrogen environment at elevated temperature. However, digestion analysis confirmed that there was insignificant change in the amount of zinc in the samples before and after the CO2 decomposition reaction. The same experiment was repeated at same configuration in order to determine the stability as well as reproducibility of the results and found approximately same conversion efficiency. Subsequently, the reaction temperature of 450 °C was regarded as the optimum temperature in order to study the origin of CO2 decomposition activity without the influence from Boudouard reaction.

Table 1. CO2 conversion and CO formation when NaY zeolite and Zn-NaY zeolite were used at different reaction temperatures.

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>CO2 conversion</th>
<th>CO formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaY</td>
<td>Zn-NaY</td>
</tr>
<tr>
<td>275</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>300</td>
<td>1.4%</td>
<td>16.1%</td>
</tr>
<tr>
<td>350</td>
<td>12%</td>
<td>47.7%</td>
</tr>
<tr>
<td>400</td>
<td>14%</td>
<td>64.7%</td>
</tr>
<tr>
<td>450</td>
<td>20%</td>
<td>70%</td>
</tr>
<tr>
<td>500</td>
<td>18.9%</td>
<td>60.5%</td>
</tr>
<tr>
<td>550</td>
<td>18.5%</td>
<td>44.7%</td>
</tr>
</tbody>
</table>

The gas composition and microscopy analyses provide strong evidence of the presence of carbon on Zn-NaY catalyst upon CO2 decomposition. Although the direct decomposition of CO2 dictates the production of oxygen as the second product, a minute but sub-stoichiometric amount of oxygen (3.7%) was detected. In addition, the conversion efficiency of CO2 decreased with time and by increasing temperature which suggests that the catalyst was deactivated, and the amount of catalytic active zinc sites was reduced. Since oxygen was produced during CO2 decomposition, it is our view that at least part of the oxygen produced was immediately consumed for the oxidation of the catalytic active metallic zinc sites and converted them into less catalytically active ZnO form. Thus, this reaction effectively reduced
the available catalytic active sites for CO₂ decomposition. Under such circumstances, the unreacted CO₂ could more readily react with carbon to form CO which was then detected in the experiments. This explains the loss of catalytic activity of Zn-NaY observed in our experiments.

Figure 1 shows the FTIR spectra of NaY and Zn-NaY before and after their use for CO₂ decomposition. The sharp and intense peaks observed between 1,200 cm⁻¹ and 450 cm⁻¹ were assigned to Si–O–Al, Si–O–Si, Si–Al, and T–O vibrational frequencies. Whereas the broad absorption band centred at 3,377 cm⁻¹ was attributed to Si–OH group and adsorbed water molecules. The peak observed at 790 cm⁻¹ was assigned to Si–O–M where M is an exchangeable metal ion species such as Na⁺ (19). It was observed that the vibrational bands corresponding to the Si–OH functional groups were absent, and this could be due to the high temperature environment during the reaction that subsequently deformed the silica tetrahedra. This was evidenced by the shift of Si–O–Al vibration from 983 cm⁻¹ to 1,002 cm⁻¹ before and after the reaction. The high temperature environment also changed the band around 3,000-3,700 cm⁻¹, which corresponds to the characteristic band of Si–OH, or adsorbed water (20). Although most of the stretching and vibrational bands were also observed at the same positions in samples after the reactions, there is one additional band that was observed at 1,498 cm⁻¹ which corresponds to stretching vibration of carbon-carbon double bonds (C=C) in aromatic molecules (21). The weak intensity of the carbon double bond (C=C) is due to the absence of hetero-atoms. The emergence of aromatic double bonds indicates the presence of carbon in the sample after the reaction. To confirm the authenticity and repeatability of the results, the same experiment was repeated and analysed with the same conditions, and the results obtained from duplicated experiments confirm the formation of carbon in the sample.
Figure 1. FTIR spectra of A: Blank Zeolite, B: Zn impregnated zeolite (Zn-NaY), C: Hydrogen reduced Zn-NaY, D: Zn-NaY after CO₂ decomposition.

The results from XRD analysis are presented in Figure 2. The blank NaY zeolite pattern contains the characteristic faujasite peaks at 6.3, 15.7, and 23.7° which corresponds to the reflections of the plane (111) [PDF-73-2310]. The addition of zinc to the zeolite structure did not cause any significant change in the zeolite diffraction patterns, which implies that zinc ions were mainly exchanged with Na⁺ ions in NaY. However, slight changes in 2θ value as well as relative intensities were observed upon the addition of zinc, which may be due to the replacement of the host metal ions in the zeolite structure by zinc. It can be concluded that the structure of NaY zeolite maintains its original crystal facets even after zinc ion-exchange. However, the intensity of the diffraction peak was reduced. As peak intensity is a function of the scattering contrast between the zeolite walls and pore channels, it decreases with the decreasing scattering contrast after the metal impregnation. Hence, the observed decrease of the diffraction peak intensity could be due to the pore filling effect imparted by zinc (22). However, the slight shift in the 2θ values after carbon dioxide decomposition is due to increase in the crystallite size by the presence of carbon in the Zn-NaY zeolite (23). In addition, the high temperature condition during the hydrogen treatment does not cause any change in the structure as X-ray diffraction studies provided strong evidence of thermal stability of the zeolites.
Figure 2. XRD patterns of A: Blank Zeolite, B: Zn impregnated zeolite (Zn-NaY), C: Hydrogen reduced Zn-NaY, D: Zn-NaY after CO$_2$ decomposition.

Figures 3 shows the SEM images and the corresponding compositional analysis of NaY, Zn-NaY, and Zn-NaY (with and without hydrogen reduction) after CO$_2$ decomposition. Neat zeolite contains sub-micron sized cube shaped particles and their macroscopic aggregates. After the zinc insertion step and hydrogen reduction at 700 °C NaY zeolite showed no change in morphology as well as the size of particles. This finding provides the evidence of thermal stability of samples up to 700 °C. When zinc was introduced into the NaY zeolite structure, this process caused a decrease of sodium content in the zeolite. However, the relative concentration of all other elements originally presented in the samples remained the same even after repeated ion exchange cycles. In addition, there was a loss of zinc in the zeolite in the sample after the hydrogen reduction most likely due to the vaporization of zinc under the combined influence of high temperature and reductive environment induced by the hydrogen. Post reaction analysis reveals that CO$_2$ decomposition changed the elemental composition of the catalyst as indicated by the change in the relative concentration oxygen and silicon. In addition, carbon was detected in these samples after the reaction. However, there were no sign of carbon on the external surface of sample. Hence, this finding complements the results provided by the FTIR which points to the generation of carbon (C=C) on the catalyst after the reaction. The presence of copper and platinum in the elemental mapping originated from the base used during sample preparation for SEM-EDS analysis.
Figure 3. SEM and its corresponding EDS of A: Blank Zeolite, B: Zn impregnated zeolite (Zn-NaY), C: Hydrogen reduced Zn-NaY, D: Zn-NaY after CO₂ decomposition.

Figure 4. Proposed reaction mechanism of carbon dioxide decomposition on Zn-NaY zeolite.
The schematics as shown in Figure 4 illustrates our proposed reaction mechanism to describe the decomposition of CO$_2$ on Zn-NaY. The Zn-NaY zeolite sample was found to decompose 70% of CO$_2$ as compared to the insignificant conversion observed for pure Na-Y zeolite under the same activation and reaction conditions. The enhanced activity observed in Zn-NaY zeolite was due to the presence of zinc and its interaction with the zeolite. Hydrogen reduction generally leads to the formation of surface oxygen vacancy site, which are beneficial for CO$_2$ activation. The adsorbed CO$_2$ acts as a soft oxidant which upon oxidation, it is converted into carbon and oxygen. Due to the close vicinity to the zinc sites, the oxygen produced immediately oxidizes the zinc sites. This was deemed to be responsible for the deactivation of the Zn-NaY catalyst over time (24).

4. Conclusions

The present study demonstrates a novel finding of using Zn-NaY zeolite to decompose CO$_2$ at relatively lower temperatures (300 – 550 °C). The results obtained from catalyst screening experiments suggest that the optimum reaction temperature occurred at 450°C at which the Zn-NaY zeolite catalyst shows a maximum conversion of CO$_2$ of 70%. The insertion of Zn inside the zeolite structure decreased the reaction temperature for CO$_2$ decomposition. SEM-EDX and FTIR have provided critical evidence to support the formation of carbon during the reaction. From these results, a plausible reaction mechanism of CO$_2$ decomposition over Zn-NaY catalysts was proposed.

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