MATERIALS CHEMISTRY COMMUNICATION

Nanophase ferrites for CO_2 greenhouse gas decomposition

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Nanophase Zn ferrites prepared by hydrothermal methods show very high efficiency for CO_2 greenhouse gas decomposition to carbon and oxygen with little or no CO as a byproduct; nanophase ferrites are highly efficient for CO_2 decomposition because this is a surface reaction and their surface to volume ratio is very high.

Climate change is probably the principal long-term problem[1] which can be caused by greenhouse gases through the so-called 'greenhouse effect'. The principal greenhouse gases are carbon dioxide, methane, nitrous oxide and perfluorocarbons. Oxides of nitrogen, carbon monoxide and non-methane volatile organic compounds (VOCs) also play a role in the greenhouse effect. Industrial expansion is substantially increasing the concentration of greenhouse gases in the atmosphere. Greenhouse gas emissions in the US alone increased by 27 million metric tons between 1990 and 1993 according to a study by the Energy Information Administration.[2] Carbon dioxide is the major component of these emissions. Thus there is a need to reduce CO_2 emissions to the atmosphere by decomposition to carbon and oxygen in order to reduce the greenhouse effect.

Previous work by Tamaura and Tabata has shown that CO_2 can be decomposed to carbon and oxygen and a minor amount of CO at a low temperature of about 300 °C by using oxygen deficient ferrites.[3] Subsequent extensive work by Tamaura and coworkers[4–12] confirmed these findings. We report here that nanophase ferrites are highly efficient for CO_2 decomposition to carbon and oxygen with little or no CO formation.

Nanophase $ZnFe_2O_4$ and $NiFe_2O_4$ were synthesized by the conventional hydrothermal method.[13] Zn and Fe nitrates were neutralized with aqueous ammonia to a pH of about 8.5 and treated in Teflon-lined Parr vessels at 178 °C for 4 h for the synthesis of $ZnFe_2O_4$. For the synthesis of $NiFe_2O_4$, Ni sulfate and Fe nitrate were neutralized with aqueous ammonia to a pH of about 7.5 and treated in Teflon-lined Parr vessels at 200 °C for 5 h. Pressure was not controlled. After the hydrothermal reaction, the solid and solution phases were separated by centrifugation. The solid phases were washed and dried before characterization by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area measurements with N_2. Powder XRD patterns (Fig. 1) showed broad peaks which indicated very small particle sizes. The XRD results were confirmed by TEM analyses which showed ferrites in the range of 5–10 nm (Fig. 2). BET surface area analyses showed that $ZnFe_2O_4$ and $NiFe_2O_4$ had very high surface areas of 168 and 151 $m^2\ g^{-1}$, respectively.

Reactivity of Zn and Ni ferrites for CO_2 decomposition was investigated after their reduction in H_2. One gram of Zn or Ni ferrite was placed in a quartz cell (20 mm in diameter and 200 mm long) and the cell was heated to 300 °C in an electric furnace while the reaction cell was evacuated. After evacuating the reaction cell for 5 min at 300 °C, hydrogen gas was passed through the ferrite sample at a flow rate of 40 ml min^{-1} for 10 min at 300 °C. After the H_2 reduction of ferrite, the reaction cell was evacuated and 1 ml of CO_2 gas was injected with a microsyringe (recorded as zero reaction time upon injection). The internal gas species were determined by gas chromatography with a thermal conductivity detector (Shimadzu model GC-8A, using Porapak Q and molecular sieve 13X as adsorbents). Results of CO_2 decomposition with Zn and Ni ferrites are shown in Fig. 3. The results clearly show that nanophase ferrites are highly effective in decomposing CO_2 to C and O_2 as indicated by the sudden drop in CO_2 partial pressure, *i.e.*, in a few seconds. Zn ferrite, which has a higher surface area than Ni ferrite, is more reactive, as expected, because of the easy access of oxygen vacancies created by reduction. In the case of nanophase Zn ferrite, little or no CO is produced while the Ni ferrite resulted in a small production of undesirable CO. A second preparation of Zn ferrite at 178 °C for 4 h also showed very high CO_2 decomposition efficiency (Fig. 4), as expected. However, this Zn ferrite showed a slightly lower CO_2 decomposition efficiency than the first preparation shown in Fig. 3, probably as a result of slight changes in particle size. The CO_2 decomposition efficiency of this Zn ferrite sample is compared with that of $CoFe_2O_4$, the latter prepared by a combustion method.[14] This $CoFe_2O_4$ has a surface area of 65 $m^2\ g^{-1}$ while $ZnFe_2O_4$ has a surface area of about 151 $m^2\ g^{-1}$ and, hence, the former is less efficient in CO_2 decomposition than the latter. Furthermore, the $CoFe_2O_4$ led to a higher fraction of CO compared to $ZnFe_2O_4$. These results show that complete decomposition of CO_2 to C and O_2 is possible through the use of nanophase ferrites because their surface-to-volume ratio is very high. Previous results with Zn ferrite of larger grain size led to not only slower decomposition but also the formation of some CO.[11] The mechanism of CO_2

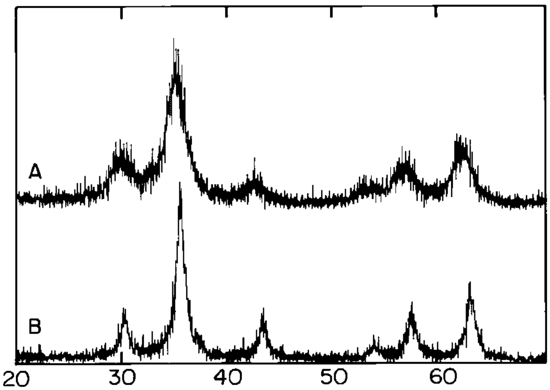

Fig. 1 X-Ray diffraction patterns of hydrothermally synthesized ferrites: (A) Zn ferrite and (b) Ni ferrite

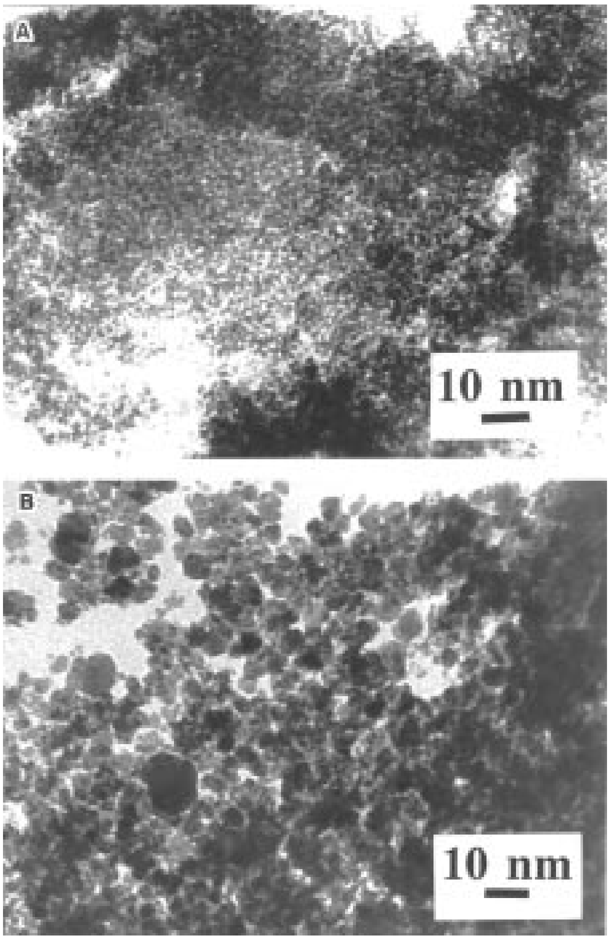

Fig. 2 Transmission electron micrographs of hydrothermally synthesized ferrites: (A) Zn ferrite and (B) Ni ferrite

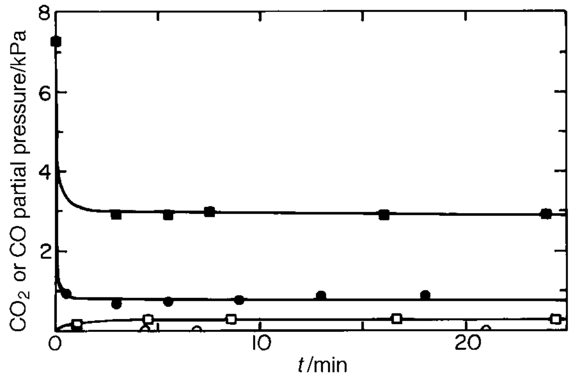

Fig. 3 Variations in the inner pressure of CO_2 (solid symbols) and CO (open symbols) in the presence of oxygen deficient Zn ferrite (circles) and Ni ferrite (squares) at 300 °C

decomposition by the oxygen deficient ferrites (ODFs) is as follows: when a nanophase ferrite is treated with H_2, it leads to the reduction of Fe^{3+} and the charge is compensated by ejecting oxygen anions (creation of oxygen vacancies) from the structure. When CO_2 comes in contact with this ODF, decomposition of CO_2 takes place by the incorporation of oxygen anions in the vacancies and deposition of carbon on the surface. The carbon on the surface can be converted to methane (methanation) upon treatment with H_2 (hydrogenation) while regenerating used ferrite to oxygen deficient ferrite. The elementary reactions involved in the decomposition of CO_2 followed by methanation are schematically shown in Fig. 5. Thus the use of nanophase ferrites leads to not only CO_2 decomposition but also production of CH_4 (methanation) which can be used as an energy source. The nanophase ferrites prepared here are also expected to be useful in the efficient trapping of H_2S, a pollutant from stationary sources such as coal power plants.

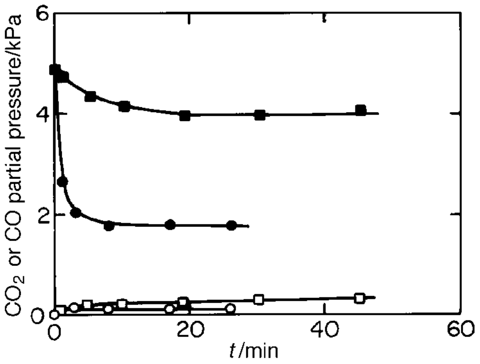

Fig. 4 Variations in the inner pressure of CO_2 (solid symbols) and CO (open symbols) in the presence of oxygen deficient Zn ferrite (circles) and Co ferrite (squares) at 300 °C

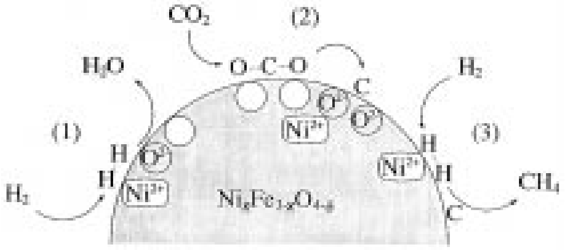

Fig. 5 Schematic of elementary reactions involved in reduction (1), decomposition of CO_2 (2) and methanation on Ni ferrite (3), as an example

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