CHEMCOMM
Communication
www.rsc.org/chemcomm

Carbon dioxide thermal system: an effective method for the reduction of carbon dioxide

Q. Chen[*ab] **and Y. Qian**[c]

[a] *Structure Research Laboratory, University of Science & Technology of China (USTC), Hefei 230026, P.R. China. E-mail: cqw@ustc.edu.cn*
[b] *Department of Materials & Engineering, USTC, Hefei 230026, P.R. China*
[c] *Department of Chemistry, USTC, Hefei 230026, P.R. China*

Received (in Cambridge, UK) 4th January 2001, Accepted 19th June 2001
First published as an Advance Article on the web 12th July 2001

When carbon dioxide is in the supercritical state and reduced by Fe_3O_4, multicarbon bearing hydrocarbon molecules such as phenol (rather than CO or formate usually formed in electrochemical or photochemical techniques) can be obtained, the reduction yield is improved remarkably and the transformation yield for CO_2 to phenol can reach 7.6%.

The reduction of carbon dioxide has been extensively studied using electrochemical[1,2] and photochemical[3–5] reactions in light of the problems of global warming and depletion of fossil fuels.[6–8] Results obtained are still not satisfactory as to useful valuable reaction products and reaction rates need to be further improved. In addition the detailed reduction mechanism could not be established in most cases. At present, much interest has focused on the use of 14-membered transition-metal microcycles in CO_2 electrochemical reduction,[9–12] however, the catalysis efficiency for these transition-metal complexes is poor and the catalyst is rapidly destroyed by hydrogenation and/or carboxylation of the microcycles.[13] On the other hand, although research to optimise the reaction products is active, multicarbon containing hydrocarbon molecules such as products containing benzene rings have never been obtained. CO is often the main reduction product while formate may also be formed depending on the reaction condition.[9,14] Photochemical CO_2 reduction has been carried out in a catalytic system using $Ru(bpy)_3^{2+}$ as the sensitizer, cobalt or nickel macrocycles as the electron relay catalysts, and ascorbate as the sacrificial reductive quencher.[3,4] These systems, however, also produce CO. Furthermore, the rate of CO_2 reduction is limited by the low mass transfer of CO_2 both in electrochemical and photochemical techniques. Hence, the conversion of CO_2 to useful products by a simple effective method is clearly an interesting and important topic in CO_2 chemistry. Here we report that, when CO_2 is in the supercritical state and reduced with Fe_3O_4 powder, it can be transformed to phenol and diphenyl ether. In some cases, we can obtain ethanol, acetaldehyde and acetic acid. This novel reduction method could allow studies of continuous reduction systems for practical industrial applications.

An autoclave (flexible Au/Ti) capable of heating the system up to 400 °C was used. A sufficient amount of solid CO_2, freshly made from high purity CO_2 gas (99+%), was placed in an autoclave to ensure that the CO_2 is in a supercritical state at high temperatures. An appropriate amount of Fe_3O_4 (chemical purity reagent) and a small amount of water obtained from the Milli-Q water purification system were placed into the autoclave (50 ml), which was heated to 100–350 °C for 1–3 h and then rapidly cooled to room temperature naturally. The vapor phase was sampled and analyzed by GC–MS, (Shimadzu, GC-MS-QP-1100EX) to detect hydrocarbons. An appropriate amount of water was placed into the autoclave, then the product was collected, and filtered. After filtration, the filtrate was analyzed by GC–MS and quantified by gas chromatography (GC), while solid products were examined by X-ray diffraction (XRD). A gas chromatograph with a flame ionization detector (GC/FID) (Ohkura, GC-202 with Porapak R column packing) was used to determine the content of the hydrocarbon molecules formed.

A typical reaction used 8.0 g CO_2, 22 g Fe_3O_4 and 0.5 ml H_2O, in which CO_2 was in excess for the oxidation of Fe^{2+} in Fe_3O_4, to ensure a high pressure in the system when it was heated to appropriate temperatures. It was found that the degree of transformation in carbon dioxide reduction increases with increasing temperature and time, and reaches a maximum value after 2.5 h treatment, then remains nearly constant. The total yield of ethanol and acetic acid was around 4.2% (mol ratio) when the reaction was carried out at 200 °C for 2.5 h and was decreased with an increase of temperature and the amount of H_2O included. However, temperatures higher than 300 °C yielded aromatic compounds with phenol and diphenyl ether being the main products with ethanol, acetic acid and acetaldehyde also present. Fig. 1(a) depicts the mass spectrum of standard phenol while that of phenol formed in the experiment

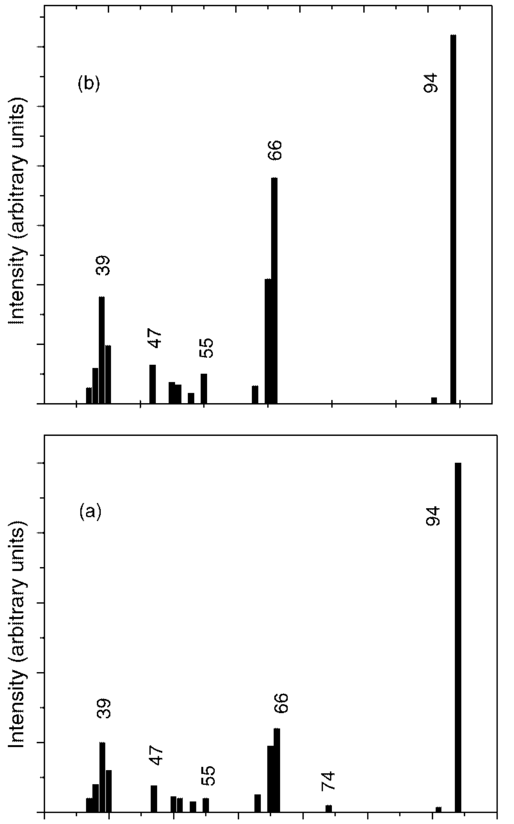

Fig. 1 Mass spectrum of phenol: (a) standard sample, (b) phenol formed *via* CO_2 reduction.

DOI: 10.1039/b100183n

is shown in Fig. 1(b). The peak at *m*/*z* 94 in Fig. 1 is assigned to the molecular ion, $C_6H_6O^+$. Almost all of the corresponding peaks in Fig. 1(a) and (b) appear at the same positions, indicating that phenol formed in the reaction. On the basis of this result, the formation of diphenyl ether in the present system can be rationalized in terms of phenol production in the carbon dioxide thermal reduction system. Crystals of phenol can be obtained by slowly heating the aqueous filtrate. A scanning electron microscope image of the sample shows the sample consists of typical grains with size 0.2 × 0.3 mm (not shown). The total yield of phenol was nearly 7.6%. The GC–MS spectrum (not shown) shows no detectable organic compounds in the starting CO_2 gas ruling out contamination in the starting material. GC analysis showed ethane, propane and isobutane, were the main products in the vapor phase, while no CO in the vapor phase or formic acid in aqueous solution was detected (the main products in electrochemical and photochemical reduction techniques). These results indicate that the mechanism of the reduction in our reaction is different from that for an electrochemical reduction process. Carbon dioxide is a low-energy molecule, with the standard potential of the $CO/CO_2^{\cdot -}$ couple in an aprotic solvent such as *N*,*N*′-dimethylformamide (DMF) containing a non ion-pairing counter cation (NEt_4^+), being as negative as -2.2 V *vs*. SCE.[13] The potential for the Fe^{3+}/Fe^{2+} redox couple is not as negative as that for the CO_2 reduction to $CO_2^{\cdot}$ anion radical. Hence reduction most probably occurs on the surface of Fe_3O_4 particles, and a surface-mediated process may be involved. The XRD pattern of the solid product shows the coexistence of Fe_2O_3 and Fe_3O_4. This is possibly due to the surface layer of Fe_3O_4 being oxidized by carbon dioxide. Furthermore, hydrocarbon molecules containing more than one carbon atom are the products, suggesting that the mechanism of this reaction could involve multielectron reductive coupling of a pair of or several carbonyls to produce an intermediate bound to the surface of the solid Fe_3O_4 particles (at Fe^{II} sites). The presence of a small amount of water is required in this reaction system as this is the source of hydrogen. Too much water, however, is unfavorable for the reduction of carbon dioxide. It has also been found that the transformation ratio increases with a decrease of Fe_3O_4 particle size, which suggests the Fe_3O_4 surface area seems to have an influence on the reaction. All these results suggest that adsorption, formation of intermediates and hydrolysis processes are involved in the reaction. More work should be carried out to establish the reduction mechanism more fully.

It is known that the rate of CO_2 reduction is limited by the low mass transfer of CO_2 both in electrochemical and photochemical techniques. Under supercritical conditions, the polarity of CO_2 can be changed by controlling its density, the dielectric constant of CO_2 ranging from 1 to 1.6.[15] The increased polarity in a high pressure system is favorable for CO_2 absorption on the surface of Fe_3O_4 particles, and may accelerate the electron transfer from Fe^{II} ions to an intermediate due to the changed adsorption energy level in the energy gap of Fe_3O_4 semiconductor. Further details about the mechanism will be discussed later. The most significant feature is that the reductant used for CO_2 reduction is easily obtained and this reaction can be performed in a continuous autoclave, which could lead to practical applications.

In conclusion, we have reported, for the first time, the reduction of carbon dioxide in the supercritical state. Valuable products such as ethanol, acetaldehyde, acetic acid and, especially, phenol can be obtained. The maximum transformation ratio for CO_2 to phenol was found to be as high as 7.6% at temperatures > 300 °C. The reduction is suggested to occur on the surface of the Fe_3O_4 particles and to occur *via* a multielectron reductive coupling of a pair of or several carbonyls to produce an intermediate. This might open a route for industrial reduction of CO_2, which previously was only viable *via* an electrochemical technique.

Notes and references

1 J. L. Roberts and D. T. Sawyer, *J. Electroanal. Chem.*, 1965, **9**, 1.
2 P. G. Russel, N. Novac, S. Srinivasan and M. Sterrinberg, *J. Electrochem. Soc.*, 1977, **124**, 1329.
3 J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos and M. Calvin, *J. Chem. Soc., Dalton Trans.*, 1987, 2105.
4 C. A. Craig, L. O. Spreer, J. W. Otvos and M. Calvin, *J. Phys. Chem.*, 1990, **94**, 7957.
5 G. M. Brown, B. S. Brunschwing, C. Creutz, J. F. Endicott and N. Sutin, *J. Am. Chem. Soc.*, 1979, **101**, 1298.
6 T. Inone, A. Fujishima, S. Konishi and K. Honda, *Nature*, 1979, **277**, 637.
7 P. G. Jessop, T. Ikariya and R. Nayori, *Nature*, 1994, **368**, 231.
8 K. R. Thampi, J. Kiwi and M. Gratzel, *Nature*, 1987, **327**, 506.
9 B. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 7361.
10 G. B. Balazs and F. C. Anson, *J. Electroanal. Chem.*, 1992, **322**, 325.
11 M. H. Schmidt, G. M. Miskelly and N. S. Lewis, *J. Am. Chem. Soc.*, 1990, **112**, 3420.
12 C. A. Kelly, Q. G. Mulazzani, M. Venturi, E. L. Blinn and M. A. Rodgers, *J. Am. Chem. Soc.*, 1995, **117**, 4911.
13 I. Bhugun, D. Lexa and J.-M. Saveant, *J. Phys. Chem.*, 1996, **100**, 19 981.
14 T. Ogata, S. Yanagida, B. S. Brunschwig and E. Fujita, *J. Am. Chem. Soc.*, 1995, **117**, 6708.
15 B. D. Drake and R. L. Smith, Jr., *J. Supercrit. Fluids*, 1990, **3**, 162.