A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C_1–C_3 selectivity

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Abstract

Photoreduction of carbon dioxide was performed using a batch reaction system. The catalysts tested were different photoactive materials of metal oxide systems supported on magnesium oxide, aluminium oxide and silicon dioxide. The conversion of carbon dioxide to C_1–C_3 compounds took place preferentially on basic oxide supported systems. Acidic oxide supported catalysts showed more selectivity to C_1 compounds. The trend of C_1–C_3 improved selectivity remained the same, irrespective of the tested photoactive material. X-ray, SEM and reflectance data revealed no change in the characteristics of the photocatalysts during the 6 h of the batch reaction. The reaction mechanism for the formation of C_1–C_3 is discussed. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The photoreduction of carbon dioxide into useful chemicals is a desirable reaction [1–11]. A long-standing goal related to the use of carbon dioxide is the dimerization of methane to form C_2 hydrocarbons such as ethane and ethylene with efficient yields and selectivity. These compounds are common feed stocks for the production of a variety of chemicals. Furthermore, the photocatalytic hydrogenation of carbon dioxide to fuels such as methane and ethylene also reduces or at least stabilises the increasing levels of atmospheric CO_2. Conversion of carbon dioxide to methane by using water and light or thermal energy

alone does not resolve the green house effect since methane is also considered to contribute to the green house effect. Therefore, it is essential to convert CO_2 to other useful substances based on C_2 and C_3 compounds. At present, the photoreduction of carbon dioxide has been developed into two conceptually different categories which utilise semiconductor electrode/colloid materials. Unfortunately, it has not yet been proved that they are clearly superior with respect to the green house problem. Furthermore, both are notoriously inefficient. Thus, it is interesting to develop catalysts that can achieve the desired carbon dioxide activation with high selectivity and extended stability. It is very well-known that acid–base properties of catalysts are important in many reactions like polymerisation, cracking, dehydration, alkyla-

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tion, halogenation and dehydrogenation [12]. Recent investigations [13] have shown that the study of the acidity of the mixed oxide systems is appropriate in order to gain a greater understanding of the physical nature of photocatalysts. Traditionally, the production of various technologically, economically and ecologically viable catalysts is based upon supported catalysts. In addition to its physical role, the support interferes either directly or indirectly with the reaction mechanism via the active phase-support interactions [14]. The aim of the present study is to prepare supported metal oxide catalyst on supports of acid/basic nature and to compare their photocatalytic behaviour. Catalysts with the same active component were prepared using various supports to establish the trend in catalytic activity. Results using three types of supports are reported. The results show that the basic nature of the support fulfills the requirement of a good photocatalyst to produce C_1 and C_2 compounds.

2. Experimental

The experiments were carried out in a well mixed heterogeneous batch type reaction. A reaction time of 6 h of irradiation was used as it was necessary for an adequate data collection. The same semiconductor material composition was supported on different oxide materials which constituted the reaction variables. In order to compare the activity of the different catalysts the active component, i.e., TiO_2 and ZnO loading was 10 wt.%. The details of the sample preparation and photoreaction of the catalysts supports of Al_2O_3 and MgO have been described earlier [15]. The catalyst support SiO_2 used was from Aldrich with a surface area of 500 m^2/g. The Pd/Al_2O_3 and Pd/SiO_2 samples (HO-11, HO-12) were from the BASF (Mannheim, Germany). Samples of 7 wt.% Li doped TiO_2 and 10 wt.% Cu doped ZnO were prepared using aqueous solutions of titanium isopropoxide, copper nitrate, zinc nitrate and lithium hydroxide. The catalysts were prepared by an impregnation method and finally calcinated at 450°C for 5 h in air. Neither formic acid nor formaldehyde was found when the experiments were conducted in the absence of CO_2, catalyst and light.

The aqueous phase was analysed for the reduction products of CO_2. Methane and ethane gases were tested by gas chromatography using a Al_2O_3 column.
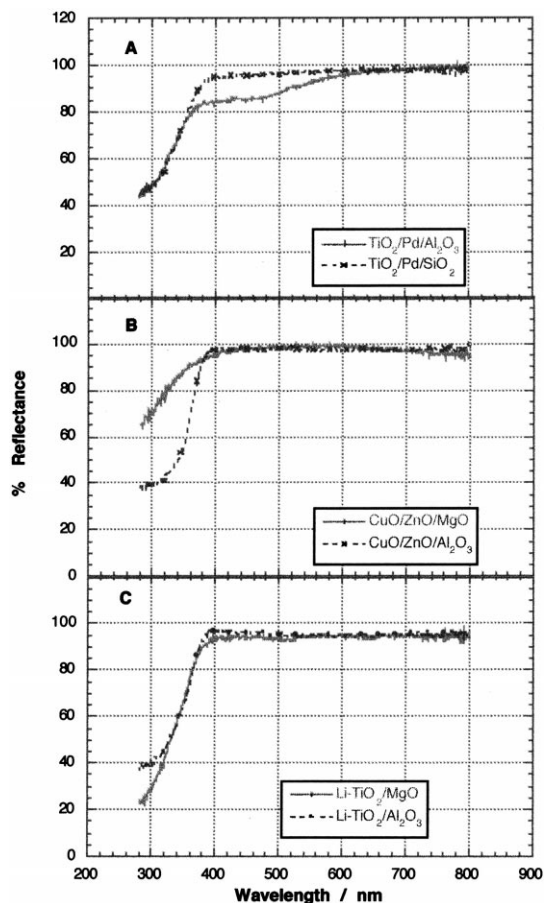

Fig. 1. Reflectance spectra of: (A) $TiO_2/Pd/Al_2O_3$ and $TiO_2/Pd/SiO_2$; (B) CuO/ZnO supported over (a) MgO, (b) Al_2O_3, (C) Li_2O–TiO_2 7 wt.% supported over (a) MgO and (b) Al_2O_3.

Methanol, ethanol and acetone were determined by gas chromatography on a Porapak Q column using a flame ionisation detector. Formic acid and formaldehyde were analysed by Nash's method [16] using a Shimadzu UV-Visible 160 spectrophotometer at chosen intervals of photo reaction time. Their amount was recalculated from the electrolyte volume in the reactor cell. Reduction was carried out in a CO_2 saturated solution of 0.5 M $KHCO_3$ (pH = 7.5), prior nitrogen degassed, under ambient conditions with a mercury arc lamp source (250 mW). Samples of catalysts after and before the reaction were analysed by X-ray, diffuse reflectance spectrophotometry and scanning electron micrograph (SEM).
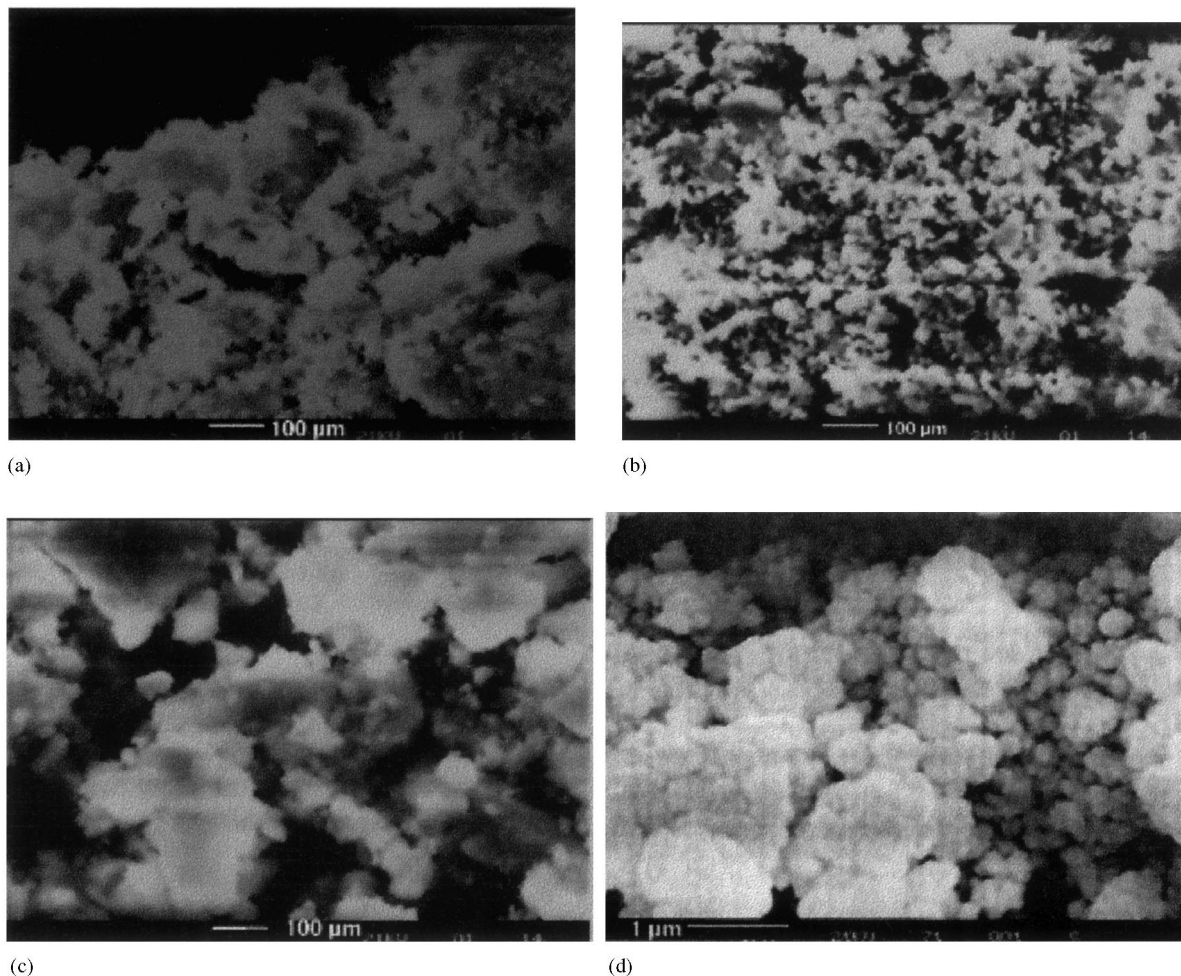
(a)

(b)

(c)

(d)

Fig. 2. Scanning electron micrography of four typical composite catalysts. (a) $TiO_2/Pd/SiO_2$; (b) $TiO_2/Pd/Al_2O_3$; (c) $CuO/ZnO/MgO$ and (d) $Li_2O–TiO_2/MgO$.

3. Results and discussion

Fig. 1(A) shows the reflectance spectra of $TiO_2/Pd/Al_2O_3$ and $TiO_2/Pd/SiO_2$ systems. Since Al_2O_3 and SiO_2 are transparent in the wavelength range between 280 and 800 nm (Fig. 1(A)) these spectra are attributable to those of the TiO_2 micro-crystals. As seen in Fig. 1(A) the reflectance spectra of both catalysts change slightly with TiO_2 impregnation. It is evident that the band gap of TiO_2 micro-crystals in Pd/Al_2O_3 and Pd/SiO_2 systems cannot be varied by changing the base support material. However, a tail between 380 and 600 nm for the system

$TiO_2/Pd/Al_2O_3$ is observed. In the case of samples prepared from CuO/ZnO (Fig. 1(B)) and Li_2O/TiO_2 (Fig. 1(C)) the spectra were not significantly different when using the different supported materials. SEM of the samples of TiO_2 impregnated BASF-catalysts CuO/ZnO and $Li_2O–TiO_2/MgO$ supported systems are shown in Fig. 2. White spots in the SEM picture show that TiO_2 microcrystals are anatase as revealed from electron diffraction analysis. The Al_2O_3 and SiO_2 matrices provide a good support for preventing aggregation of TiO_2 particles.

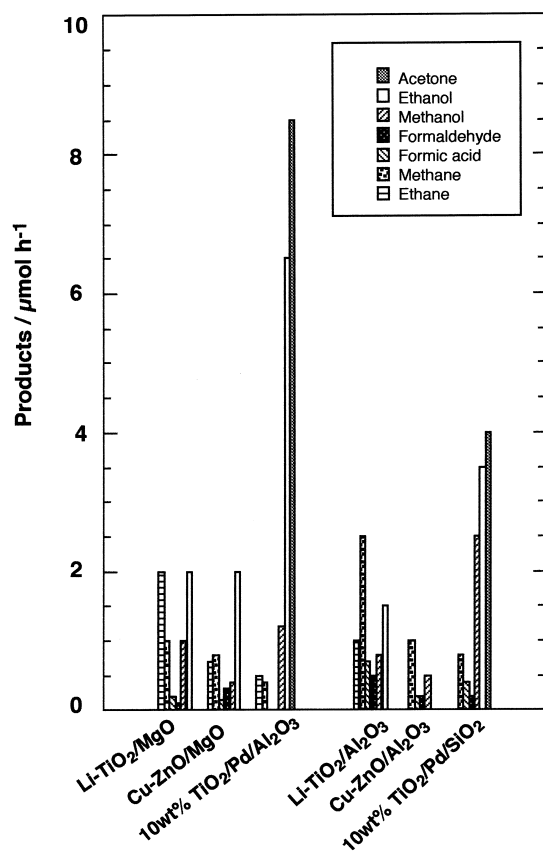The results of the irradiation of carbon dioxide photoactive material supported catalysts are sum-

Fig. 3. The carbon dioxide photoreduction products obtained by irradiation of various acid and basic supported oxides in CO_2 saturated solutions.

marised in Fig. 3. No product was obtained under otherwise identical conditions but without active component or without illumination. The fact that no product was formed with bear supports indicates that the reactivity of adsorbed CO_2 is negligible. The samples of BASF commercial catalysts of Pd/Al_2O_3 and Pd/SiO_2, which are used for commercial production of ethylene hydrogenation, were examined for CO_2 reduction with and without TiO_2 impregnation. There was no formation of CO_2 photoreduction products on the bare samples of Pd/Al_2O_3 and Pd/SiO_2 systems. The effects of TiO_2 impregnated samples showed a measurable photocatalytic activity. There was also a difference between the activity of titanium dioxide impregnated with Pd/Al_2O_3 and Pd/SiO_2 catalysts for C_1–C_3 compound formation. CO_2 conversion to C_1–C_3 compounds over these materials was specific

over $TiO_2/Pd/Al_2O_3$. The products were 0.4 μmol/h of CH_4 and 0.5 μmol/h of C_2H_6 whereas in the $TiO_2/Pd/SiO_2$ system 0.8 μmol/h of CH_4 were formed with no C_2H_6. This shows the role of SiO_2 acid–base material support in the product selectivity compared to Al_2O_3 supported systems. In contrast to this, the bulk Pd/TiO_2 system exhibited a very high selectivity for the production of methane from the photoreduction of CO_2 [17]. The deposition of various metals can lead to the formation of C_2 and C_3 compounds as reported earlier [17–20]. In the present case the nature of the support itself changes the selectivity to C_1 and C_2 compounds. Paul and Hoffmann [21] suggested that the lowered work function of an alkali promoted surface facilitates a high probability of electron transfer to impinge neutral CO_2 molecules. Furthermore, they proved that the dimerization occurs via a radical–substrate reaction mechanism in a hydrogen deficient system. In addition a change in the product distribution was seen over the majority of the bulk and other photoactive compounds compared to the present supported systems (Fig. 3). The mixture of CuO/ZnO 10 wt.% is known to be a catalyst for the synthesis of methanol. We chose this system to study its photocatalytic activity. The formation of CH_4 and C_2H_6 were found to be 0.8 and 0.7 μmol/h over CuO/ZnO supported on MgO. In the case of Al_2O_3 supported systems there is no formation of C_2H_6 but of 1.0 μmol/h of CH_4. Similarly, Li_2O/TiO_2 7 wt.% is taken here over different supports for the test reaction. Kiwi and Morrison reported [22] a profound effect of lithium-doping TiO_2 anatase. It promotes conduction band electron transfer and enhances the photogeneration of hydrogen in water cleavage reaction. Our results suggested that other than the role of support dopant for ZnO and TiO_2, i.e., Cu and Li cause an increase in the total number of basic sites. The radius of Cu (0.93 Å) is larger than that of the Zn (0.74 Å) ion and therefore, the introduction of Cu ion into the lattice of ZnO is expected to cause a distortion of ZnO. Thus creating a low co-ordinated oxygen species which leads to an increase in the basic nature of the catalyst. The incorporation of a basic lithium oxide in TiO_2 generates relatively stronger basic sites of TiO_2 alone due to the suppression of acidic sites. Thus the C_1 and C_2 selectivity obtained over these catalysts is more specific than that of the higher acidic supported based systems. This suggests
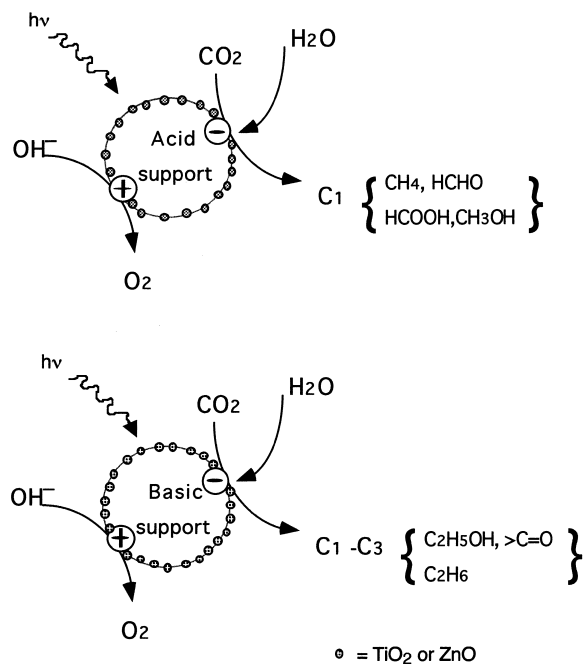
Fig. 4. Schematic model showing the photoinduced process of an acid and basic oxide supported catalysts.

that though the basic nature of the support is of fundamental importance, it is not alone responsible for controlling the selectivity during this photo reduction. The data obtained do not discriminate among alternative mechanistic models and it is thus only possible to speculate over the possible options. The representation of the probable reaction process is shown below; however, further examinations are necessary to elucidate the detailed mechanism. Therefore, we propose the following scheme:

The absorption of photons with energy higher than the TiO_2 and ZnO band gap generates electron–hole pairs according to Eq. (1),
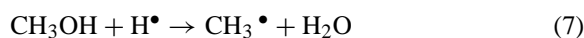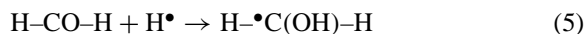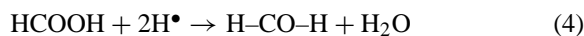
$$M_xO_y \xrightarrow{h\nu} e^- + h^+ \tag{1}$$

The absence of dissolved molecular oxygen, can only favour the reduction reaction of protons to form radicals,

$$H^+ + e^- \rightarrow H^\bullet \tag{2}$$

Considering that holes are being consumed by water, see Fig. 4, the pathway of CO_2 fixation via $H^\bullet$ radicals

leading to methane formation (eight electrons charge transfer) can be writen as follows

$$CO_2 + 2H^\bullet \rightarrow HCOOH \tag{3}$$

$$HCOOH + 2H^\bullet \rightarrow H\text{–}CO\text{–}H + H_2O \tag{4}$$

$$H\text{–}CO\text{–}H + H^\bullet \rightarrow H\text{–}{}^\bullet C(OH)\text{–}H \tag{5}$$

$$H\text{–}{}^\bullet C(OH)\text{–}H + H^\bullet \rightarrow CH_3OH \tag{6}$$

$$CH_3OH + H^\bullet \rightarrow CH_3{}^\bullet + H_2O \tag{7}$$

$$CH_3{}^\bullet + H^\bullet \rightarrow CH_4 \tag{8}$$

Furthermore, the recombination of $CH_3{}^\bullet$ in [7] may lead to C_1 and C_2 formation

$$CH_3{}^\bullet + CH_3{}^\bullet \rightarrow C_2H_6 \tag{9}$$

The difference in the kind of products between the bulk mixtures reported by others and ours may have resulted from differences in the nature of the support used for the active component. As in other cases, the difference in experimental conditions using either a gas phase or liquid phase or at pressure may be postulated. The effects of changes in experimental variables, the concentration of the active photocomponent, the amount of catalyst used, the design of the reactor, type of mode of test unit (batch or continuous) are the subjects to improve the activity and selectivity. Research is under way in order to elucidate these points. Thus, the results have been compared in an attempt to establish the trend. In particular we have looked at effects of using a basic or acid supports on the photocatalytic activity of CO_2 reduction. The interplay among susbtrate, semiconductor and metal particles towards the photoelectrocatalytic reactions reported here, show to some extent the photoelectronic interaction in the systems.

4. Conclusions

It can be concluded from the data obtained that the catalyst support plays an essential role in the observed selective photoreduction of CO_2 to C_1–C_3 compounds (Fig. 4). The selectivity exhibited by the $TiO_2/Pd/Al_2O_3$ system is quite noteworthy in relation

to other semiconductor based systems which generate a broad distribution of products. The nature of the support favours CO_2/HCO_3^- photoreduction to C_1–C_3 products. The basic nature of the support proved to be more suitable for the activity and selectivity of the catalyst for C_1–C_3 compounds than the acid nature of the support. Furthermore, carbon dioxide solubility is another factor that has to be taken into account, mainly in aqueous solutions.

Acknowledgements

References

[1] V. Heleg, I.Willner, J. Chem. Soc., Chem. Commun. (1994) 2113.

[2] S. Kaneco, H. Kurimoto, K. Ohta, T. Mizuno, A. Saji, J. Photochem. Photobiol. A 109 (1997) 59.

[3] H. Yoneyama, Catal. Today 39 (1997) 169.

[4] A.M. Braun, D.G. Skolmick, Chimia 42 (1988) 104.

[5] K.R. Thampi, A.J. McEvoy, M. Grätzel, in: C M Pradier, J. Paul (Eds.), Carbon Dioxide Chemistry: Environmental Issues (1994) 375.

[6] H. Uchida, T. Sasaki, K. Ogura, J. Mol. Catal. 93 (1994) 269.

[7] M. Watanabe, Surf. Sci. Lett. 279 (1992) L236.

[8] J. Melsheimer, W. Guo, D. Ziegler, M. Wesemann, R. Schlögl, Catal. Lett. 11 (1991) 157.

[9] J.T.S. Irvine, B.R. Eggins, J. Grimshaw, Solar Energy 45 (1990) 27.

[10] F. Solymosi, I. Tombacz, Catal. Lett. 27 (1994) 61.

[11] K. Ogura, M. Kawano, J. Yamo, Y. Saka, J. Photochem. Photobiol. A Chem. 66 (1992) 91.

[12] H. Noller, J.A. Lercher, H. Vinek, Mat. Chem. Phys. 18 (1988) 577.

[13] J. Papp, S. Soled, K. Dwight, A. Wol, Chem. Mat. 6 (1994) 496, and references 45 and 47 therein.

[14] H.V. Damme, Supports in photocatalysis, in: N. Serpone, E. Pellizetti (Eds.), Photocatalysis Fundamentals and Applications, Wiley, New York, 1989, p. 175.

[15] M. Subrahmanyam, V.T. Supriya, P. Ram Reddy, Int. J. Hydrogen Energy 21 (1996) 99.

[16] M. Ulman, A.H.A. Tinnemans, A. Mackor, B. Aurian-Blajeni, M. Halmann, Int. J. Solar Energy 11 (1982) 213.

[17] O. Ishitarri, C. Inoue, Y. Suzuke, T. Ibusuki, J. Photchem. Photobiol. A Chem. 72 (1993) 269.

[18] M. Watanable, Surf. Sci. Lett. 279 (1992) L236.

[19] J.T.S. Irvine, B.R. Eggins, J. Gimshaw, Solar Energy 45 (1990) 27.

[20] M.M. Taqui Khan, D. Chatterjie, J. Bhatt, Proc. Indian Acad. Sci. (Chem. Sci.) 104 (1992) 747.

[21] J. Paul, F.M. Hoffmann, Catal. Lett. 1 (1988) 445.

[22] J. Kiwi, C. Morrison, J. Phys. Chem. 88 (1984) 6146.