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CO_2 hydrogenation over Pd-modified methanol synthesis catalysts

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Abstract

The effect of palladium incorporation on the performance of Cu–ZnO(Al_2O_3) during the hydrogenation of carbon dioxide has been assessed. Temperature-programmed reduction profiles and X-ray photoelectron spectra of copper revealed that Pd enhances copper oxide reduction. Carbon dioxide conversion and methanol yield were found to increase on Pd-loaded catalysts. The importance of the palladium incorporated to the base Cu–ZnO(Al_2O_3) catalyst in determining the catalytic activity is discussed in terms of the relative ease with which hydrogen is dissociated on the Pd particles and then spilt over the Cu–ZnO phase of the base catalyst. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon dioxide emissions in the atmosphere through industrial activities and the options for recycling CO_2 for useful purpose are of prime interest nowadays. Chemical conversion of CO_2 into raw chemicals, e.g. methanol, appears as one of the most attractive processes [1]. Methanol is a raw chemical of great interest because of its many applications in fuel and chemical industries. Its synthesis is currently carried out over ZnO-supported Cu catalysts promoted with Al_2O_3, starting from a mixture of CO, CO_2 and H_2. Many studies have recently appeared that aim at identifying whether or not it would be possible to obtain not just higher catalytic activities but to replace CO by CO_2 in the reaction feed while maintaining high and stable activity. Methanol synthesis from $CO_2 : H_2$ mixtures also adds the incentive to use CO_2, one of the gases responsible for the greenhouse effect, as a carbon source for methanol. It has been found that copper catalysts can be promoted for methanol synthesis from $CO_2 : H_2$ feed by incorporating a second catalyst, in which the active phase is constituted of Pd particles, as a physical mixture [2–4]. The enhancement of catalytic activity in these physical mixtures has been assigned to hydrogen spillover from metallic palladium to the Cu–ZnO(Al_2O_3) particles which maintains the copper in a reduced state [2,5–7]. It has recently been reported that promotion of methanol synthesis from $CO_2 : H_2$ feed can also be obtained with Pd-impregnated Cu–ZnO(Al_2O_3) catalysts [6,7]. Moreover, activity and stability of the methanol synthesis catalysts appear to be greatly influenced by feed composition. As a general tendency, ZnO-supported Cu catalysts deactivate faster by feeding $CO_2 : H_2$ mixtures than in a $CO : CO_2 : H_2$ stream. In this contribution, the catalytic performance of Pd-contain-

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ing Cu/ZnO catalysts for the high pressure hydrogenation of carbon dioxide is reported to aid the understanding of some steps involved in the conversion of CO_2 to methanol.

2. Experimental

A copper–zinc–alumina (CZA) catalyst, with a nominal composition of Cu : Zn : Al=55 : 30 : 15 (atomic), was prepared by coprecipitation of the corresponding metal nitrates at constant pH (ca. 7.0) and at constant temperature (323 K) [8]. The precipitate was washed with deionized water, dried overnight at 383 K and, finally, calcined in air at 623 K for 4 h. The powder catalyst was then pelletized and sieved (0.40–0.52 mm) for catalytic experiments and catalyst characterization. Two Pd-containing catalysts were prepared by impregnation of the base CZA sample with $Pd(NO_3)_2$ solutions of appropriate concentrations to obtain Pd loadings of 5.0 and 10.0 wt% PdO, and removing the excess water in a rotary evaporator.

Temperature-programmed reduction (TPR) experiments were carried out in a semiautomatic Micromeritics TPD/TPR 2900 apparatus interfaced to a microcomputer. TPR profiles were obtained by passing a 10% H_2/Ar flow (50 cm^3/min) through the sample (ca. 30 mg). The temperature was increased from room temperature to 773 K at a rate of 10 K/min, and the amount of H_2 consumed was determined with a TCD; the effluent gas was passed through a cold trap placed before the TCD in order to remove water from the exit stream. Prior to H_2 flow, the sample was dried by passing N_2 at 373 K at a rate of 100 cm^3/min.

X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and MgK_α ($h\nu$=1253.6 eV) X-ray source. The samples were either outgassed at room temperature or reduced in H_2 at 553 K for 1 h within the pretreatment chamber of the spectrometer. The intensities of Cu 2*p*, Zn $2p_{3/2}$, Al 2*p* and Pd 3*d* peaks were estimated by calculating the integral of each peak after smoothing and subtraction of the S-shaped background and fitting the experimental curve to a combination of Gaussian and Lorentzian lines of variable proportion. The binding energies (BE) were referenced to the C 1*s* peak at 284.9 eV, this reference giving BE values with an accuracy of ±0.1 eV.

Activity tests were carried out using a stainless-steel fixed-bed flow reactor. The reaction was conducted at 40 bar overall pressure ($H_2 : CO_2$=3 : 1 molar), reaction temperatures in the range 433–473 K and contact time W/F=0.2 g h/mol, the flow being controlled by means of electronic mass-flow controllers. The effluents of the reactor were analyzed on-line by a Hewlett–Packard 5730 A gas chromatograph. To avoid condensation of the reaction products, outlet lines were heated at 423 K. The GC was equipped with a Poraplot Q and Molecular Sieve X5A columns. Analysis of the products was carried out with a TCD, which covers the analysis of CO, CO_2 and H_2O, using an FID for the analysis of hydrocarbons and oxygenates.

3. Results and discussion

3.1. Catalyst characterization

The TPR profiles of the two Pd-loaded catalysts and the reference CZA are shown in Fig. 1. The TPR profile of catalyst CZA displays the maximum H_2-consumption rate at 500 K, and shifts to 484 and 458 K for catalysts 5.0 and 10.0% PdO, respectively. This peak is assigned to reduction of CuO to metallic copper. Moreover, Pd-containing catalysts exhibit other low-temperature peaks, at ca. 360 K, of very low intensity, for 5% PdO and at 375 K for the 10.0% PdO counterpart, which is attributed to a reduction of palladium oxide to Pd metal. A third broad reduction peak around 400 K is also observed for the 10% PdO-promoted sample. The enhancement of CuO reduction in the Pd-loaded samples is explained on the basis that hydrogen is easily dissociated on Pd metal particles and then spilt on the surface of other phases. Looking at these TPR profiles, it is clear that temperatures around 540 K are required to completely reduce copper oxide phases. These results were conclusive in defining the activation temperatures of the catalysts. According to the results displayed in Fig. 1, the calcined catalysts were reduced within the catalytic reactor at 553 K in a 10% H_2/Ar stream for 4 h prior to catalytic measurements.

Photoelectron spectroscopy was used to study the chemical state of the elements and their relative abundance at catalyst surfaces. The BE values of core

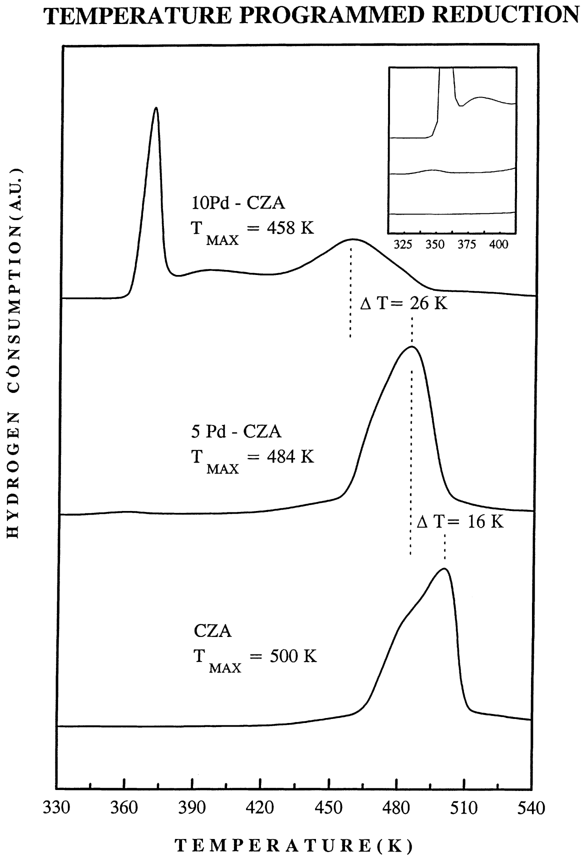

Fig. 1. TPR profiles of CZA and Pd-loaded CZA catalysts.

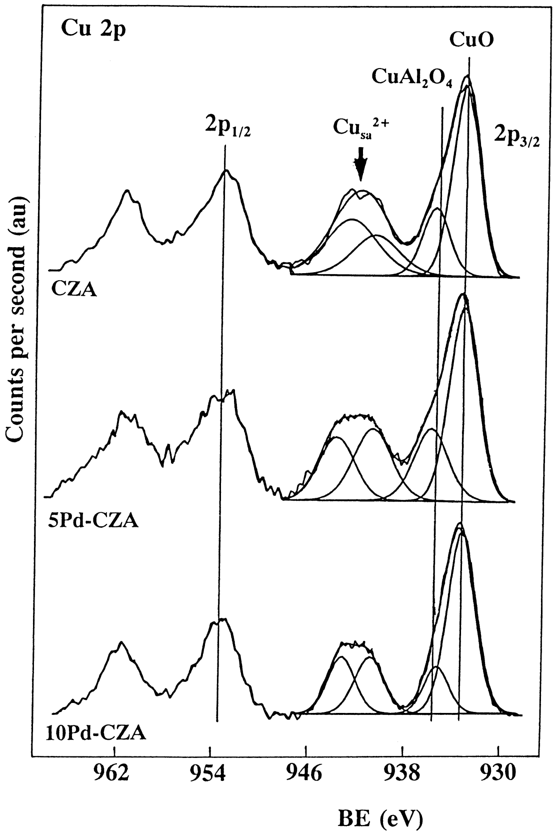

Fig. 2. Cu $2p$ core level spectra of outgassed catalysts.

electrons and surface atomic ratios for CZA and Pd-loaded catalysts are summarized in Table 1. For the sake of clarity, and in order to have an idea of peak profile, the Cu $2p$ core levels of calcined and H_2-reduced catalysts are displayed in Figs. 2 and 3, respectively. The Cu $2p$ line profile changes dramatically upon H_2-reduction at 553 K. The calcined and outgassed samples (Fig. 2) display the principal Cu

Table 1
Binding energies (eV) of core electrons and surface XPS atomic ratios of catalysts [a]

Pretreatment	Cu $2p_{3/2}$	Pd $3d_{3/2}$	Zn $2p_{3/2}$	Cu/Zn	Cu/(Zn+Pd)
CZA, vac	933.4 (73) 935.8 (27)	—	1022.0	1.292	1.292
CZA, Tr=553 K	932.5	—	1022.0	1.119	1.119
5.0%Pd–CZA, vac	933.4 (69) 936.0 (31)	335.3 (61) 337.2 (39)	1022.1	0.938	0.550
5%Pd–CZA, Tr=553 K	932.4	335.1	1022.1	0.727	0.455
10%Pd–CZA, vac	933.4 (82) 935.5 (18)	335.4 (39) 336.7 (61)	1022.0	0.699	0.452
10%Pd–CZA, Tr=553 K	932.4	335.1	1022.1	0.533	0.343

[a] Values in parenthesis are peak percentages.

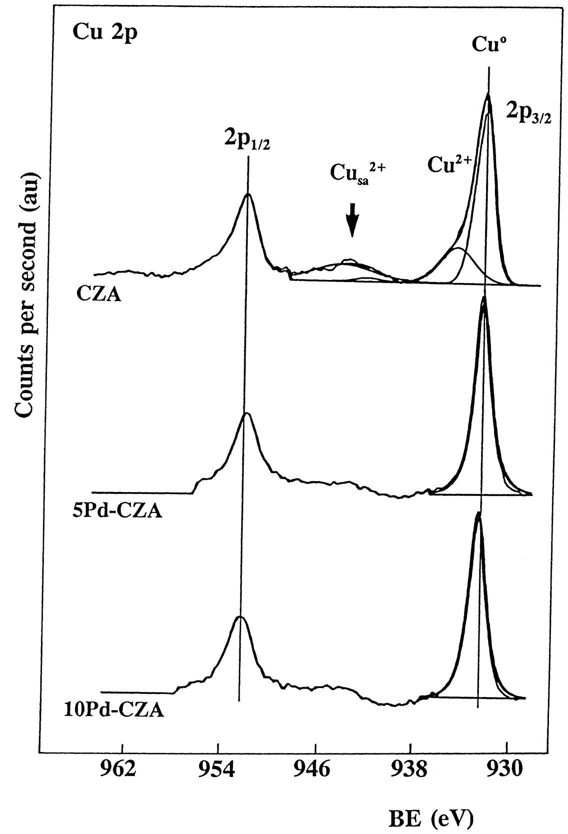

Fig. 3. Cu $2p$ core level spectra of H_2-reduced catalysts.

$2p_{3/2}$ peak somewhat above 934 eV, which is characteristic of Cu^{2+} species. These values are in agreement with those obtained by other groups [9,10]. An additional means of identifying Cu^{2+} ions is the satellite peak, which is caused by electron shake-up processes. The origin of the satellite peaks is considered to be the promotion of $3d$ electrons to $4s$ and/or $4p$ levels or, alternatively, to be a charge transfer of ligand electrons to unfilled $3d$ orbitals. This transfer cannot occur in Cu^{+} and Cu^{0} because of their completely filled $3d$ shells. The large value of the FWHM of Cu $2p_{3/2}$ peak for calcined samples and its asymmetry in the high binding-energy side suggest that the Cu $2p_{3/2}$ peak of Al-containing samples in this work may consist of more than one contribution. On this basis, peaks on calcined samples have been deconvoluted into two contributions centered at around 933.5 and at 935.5–936.0 eV. The weight percentage corresponding to the area under each peak is also tabulated in Table 1. The peak at 935.5–936.0 eV is assigned to Cu^{2+} in a $CuAl_2O_4$ spinel-like environment [11], and the peak at 933.4 eV is attributed to Cu^{2+} in CuO. The disappearance of the satellite peak and the simultaneous shift of the principal Cu $2p_{3/2}$ peak towards lower BE upon H_2-reduction at 553 K lead to the conclusion that the copper species are Cu^{+} or Cu^{0}, but in no case Cu^{2+}. Since the BE values and widths for Cu $2p$ peaks in cuprous oxide (Cu^{+}) are almost identical to those in Cu^{0}, differentiation between reduced copper species is impossible from XPS alone. As has been well documented, the distinction between Cu^{+} and Cu^{0} species present in the catalyst is only feasible through examination of the modified Auger parameter. The modified Auger parameter is defined by the equation: $\alpha_{A'}=h.\nu+(Cu_{LMM}-Cu\ 2p)$, where $\alpha_{A'}$ represents the difference between the kinetic energy of the Cu_{LMM} Auger electron and the Cu $2p_{3/2}$ photoelectron. Addition of the energy of the incident photon allows for the modified Auger parameter to be independent of the excitation energy. The $\alpha_{A'}$ values at 1851.1−1851.3 eV are indicative of the presence of Cu^{0} species [12].

The Pd-containing catalysts exhibit two Pd $3d_{5/2}$ components: the first one with a BE of 337.2 or 336.7 eV, which is typical of PdO species [13,14], and a second at 335.3 or 335.4 eV which is associated to Pd^{0}. Upon exposure to H_2 at 553 K, the oxide becomes completely reduced as only one peak at 335.1 eV, due to Pd^{0}, is observed. Some alloying of Pd with Zn, at the ZnO interface, cannot be ruled out as a certain broadening of the Pd $3d$ peaks is detected in the high BE side of the principal peaks.

The surface Cu/Zn and Cu/(Zn+Pd) atomic ratios have been calculated from peak areas and atomic sensitivity factors [15]. Both Cu/Zn and Cu/(Zn+Pd) ratios drastically decrease when Pd is added to the base CZA sample and, to a lesser extent, upon reduction. The decrease of the Cu/Zn and Cu/(Cu+Pd) atomic ratios in Pd-loaded samples indicates that the exposed copper atoms are covered by Pd particles. The subsequent decrease of these ratios for the H_2-reduced counterparts clearly indicates a lack of copper dispersion as a consequence of Cu particle formation from phases, where Cu^{2+} is dispersed on an oxide substrate. The loss of Cu dispersion during reduction appears to be related to the rather low Tamann's

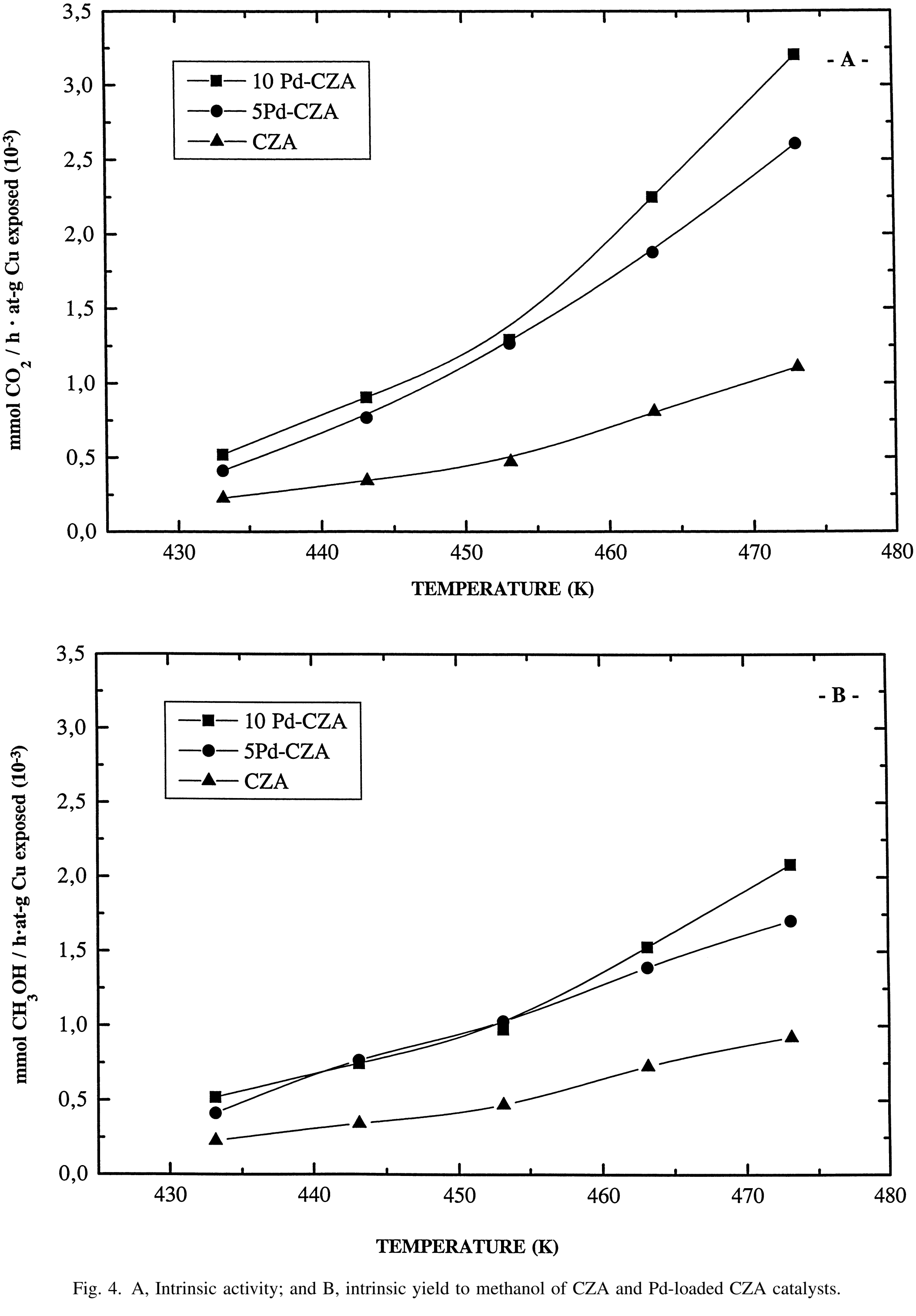

Fig. 4. A, Intrinsic activity; and B, intrinsic yield to methanol of CZA and Pd-loaded CZA catalysts.

temperatures (T_M) of copper (at which the mobility of the copper on catalyst surface becomes significant).

3.2. Activity measurements

The reaction of CO_2 and H_2 produced methanol and water, with CO only at temperatures >453 K. In order to account for the covering of the Cu particles by Pd atoms, the rate of CO_2 conversion and methanol yield (mmol/h (at-g)Cu) were divided by the Cu/(Zn+Pd) atomic ratio, measured by XPS. Such values are given in Fig. 4(A and B) as functions of the reaction temperature for all the catalysts.

The incorporation of Pd to the base Cu–ZnO(Al_2O_3) catalyst enhance the CO_2 conversion to methanol at all the temperatures and times-on-stream investigated. The promotion in methanol formation was found to be independent of the Pd loading in the two Pd-loaded catalysts, suggesting that Pd does not act as independent catalytic site for methanol synthesis. This conclusion is validated when considering the similar Pd dispersions, derived from the Pd/Zn XPS intensity ratios, for Pd-containing catalysts. Fig. 4(B) shows the methanol yield as a function of the reaction temperature for all the catalysts. Comparison of these data with that reported in Fig. 4(A) indicates that CO_2 becomes converted into CO by the reverse water–gas shift reaction ($CO_2+H_2 \Leftrightarrow CO+H_2O$) at temperatures >450 K.

4. Conclusions

Carbon dioxide hydrogenation was promoted in Pd-containing Cu–ZnO(Al_2O_3) catalyst. For the two Pd loadings (5.0 and 10.0% PdO) explored, the intrinsic activity for this reaction was essential. As revealed by TPR and XPS, the enhancement of copper oxide reduction by Pd and its promotional effect on CO_2 hydrogenation support the proposal that hydrogen spilt from Pd is responsible for the increase in methanol production. The spillover would balance the oxidizing effect of water, and/or CO_2, at the Cu surface.

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