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Hydrogenation of carbon dioxide to methanol over palladium-promoted $Cu/ZnO/Al_2O_3$ catalysts

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Abstract

The effect of Pd on a $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis from CO_2/H_2 has been investigated. Activities of impregnated catalysts and physical mixtures were studied in an internal recycle reactor under 5 MPa, 250°C and a range of conversions. In all cases, the promotion of methanol production was greater at higher flow rates (lower conversions). The promotion achieved by use of $Pd/Al_2O_3 + Cu/ZnO/Al_2O_3$ physical mixtures was found to increase with Pd content. Greater promotion was observed over the Pd impregnated $Cu/ZnO/Al_2O_3$ catalysts, although this was insensitive to the particular Pd loadings used. The results are consistent with the proposal that hydrogen spillover is responsible for the observed promotion. The effectiveness of Pd as a promoter for the reduction of CuO in the catalysts was studied by TPR and was found to be related to the level of promotion in methanol production.

Keywords: CO_2 hydrogenation; Pd catalysts; Methanol production

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1. Introduction

The recognition that the hydrogenation of carbon dioxide to methanol is a promising approach to the recycling of emitted CO_2 has given rise to considerable interest in the development of selective catalysts. Inui and coworkers [1-3] have developed a two-stage process for the conversion of CO_2 to gasoline via methanol. In this context, they have investigated the effect on methanol synthesis of Rh, Ru, Pd and Ag addition to Cu/ZnO-based catalysts. Pd and Ag were found to promote significantly methanol synthesis from CO_2. In these studies, the promoting metals supported on Al_2O_3 were incorporated in physical mixtures and, since Pd/Al_2O_3 and Ag/Al_2O_3 did not show any activity for methanol synthesis from CO_2, it was concluded that the mechanism of promotion was by hydrogen spillover which served to maintain a reductive state of Cu. Subsequently, Fujimoto and Yu [4], investigating the effect of Pd and Pt on Cu/ZnO-based catalysts, arrived at a similar conclusion and in addition demonstrated the stability of the Pd promoted catalysts against poisoning of methanol synthesis activity by water. Lanthanide oxides [5] and TiO_2 [6] have also been shown to promote CO_2 conversion to methanol over Cu/ZnO-based catalysts, while Ag promotes Cu/ZrO_2 [7] and Pd on other supports has also been investigated [8-10].

There is also interest in methanol synthesis

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Table 1
Compositions and surface areas of the calcined catalysts

Catalyst	Pd/Cu (atomic ratio)	PdO (wt.-%)	CuO (wt.-%)	ZnO (wt.-%)	Al_2O_3 (wt.-%)	BET surface area (m^2/g)
Cu/Zn/Al-1	0	0	60.3	28.6	10.8	115
Cu/Zn/Al-2	0	0	60.1	28.3	11.3	112
0.04 Pd/Cu/Zn/Al	0.04	3.7	58.2	27.2	10.7	112
0.09 Pd/Cu/Zn/Al	0.09	7.7	55.6	25.7	10.6	110
0.07 Pd/Al + Cu/Zn/Al [a]	0.07	4.0	36.2	17.2	42.5 [b]	–
0.21 Pd/Al + Cu/Zn/Al [a]	0.21	12.0	36.2	17.2	34.5 [b]	–

[a] Compositions and surface areas of the Pd/Al were not determined; nominal compositions of Pd/Al were used to calculate the compositions of physical mixtures.

[b] Includes the Al_2O_3 in the PdO/Al_2O_3 component of the physical mixtures.

from existing process plant operating with CO_2-enriched synthesis gas [11]. The difficulties include increased catalyst deactivation at high CO_2 levels and matrix instability arising from water production. The promoted Cu/ZnO-based catalysts may find application in this context.

In the study reported here, the effect of Pd on an industrial type $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis from CO_2/H_2 has been investigated under industrial conditions (5 MPa, 523 K) in an internal recycle reactor, with the experiments carried out at a wide range of conversions. A comparison has been made between incorporation of Pd by impregnation and addition of Pd via physical mixtures of $Pd/Al_2O_3 + Cu/ZnO/Al_2O_3$ to assess the importance of hydrogen spillover in this catalyst system.

2. Experimental

$CuO/ZnO/Al_2O_3$ (Cu/Zn/Al) catalysts were prepared by two-stage precipitation according to a proprietary recipe [12]. The dried

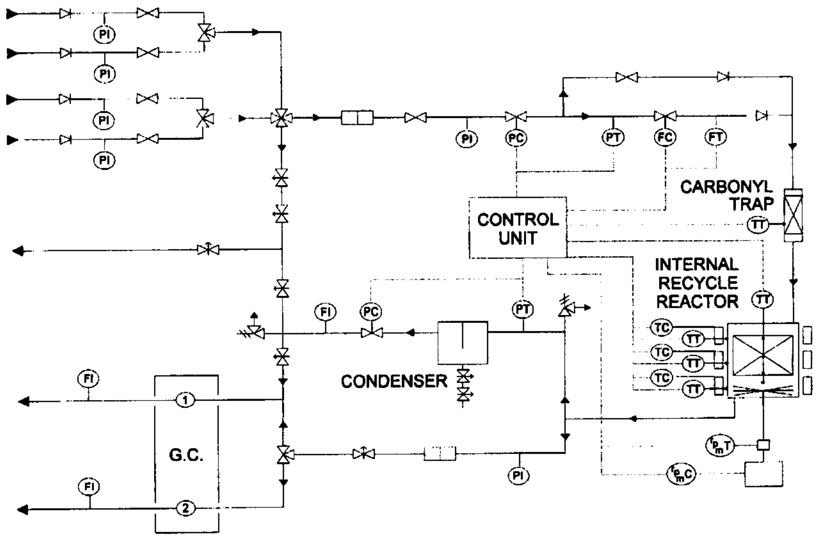

Fig. 1. Internal recycle reactor system.

precipitate was calcined in air at 300°C for 6 h. After the addition of 2% (w/w) graphite for binding, pellets of 2 g/cm^3 density were formed. These were crushed and sieved to a particle size range of 250–500 μm. Prior to reaction, the catalyst was activated in situ by reduction of the CuO in the catalyst under flowing 5% H_2 in N_2 at 215°C.

$PdO/CuO/ZnO/Al_2O_3$ (Pd/Cu/Zn/Al) catalysts were formed by impregnation of the precipitate produced above before calcination. The dried precipitate was reslurried in dilute Na_2CO_3 before neutralising with $Pd(NO_3)_2$ solution. The quantities of Na_2CO_3 and $Pd(NO_3)_2$ were pre-calculated to achieve the desired Pd loadings. For the physical mixtures, PdO/Al_2O_3 (Pd/Al) was prepared by precipitation of Pd aluminate, followed by calcination. The calcined Pd/Al and Cu/Zn/Al powders were thoroughly mixed before pelletisation. These catalysts were also crushed to 250–500 μm particle size. Metal compositions of the calcined catalysts were determined by AA spectrophotometry and are given in Table 1. Throughout this paper, Pd loadings refer to the Pd:Cu atomic ratio shown in Table 1. BET surface areas were determined using a Micromeritics ASAP 2000.

Kinetics were measured in an internal recycle gas phase flow reactor (Fig. 1). The impeller speed (set at 1500 rpm), temperature, pressure and flow were fully computer controlled. Industrial conditions of 5 MPa and 250°C were used. The synthesis gas was a 4 H_2:1 CO_2 mix. The flow rate (defined as mol (of synthesis gas) h^{-1} g_{Cu}^{-1} (Cu as measured by A.A. spectrophotometry)) was varied to achieve different conversions. 10% He was added to the synthesis gas as an internal analytical standard. Product analysis was performed by on-line gas chromatography, making use of a Poropak Q Column and a TCD.

The temperature programmed reduction (TPR) of calcined catalysts was performed at a heating rate of 10°C/min under flowing 5% H_2 in argon. The consumption of H_2 due to the reduction of PdO and CuO was monitored using a TCD.

3. Results and discussion

The reaction of CO_2/H_2 produced methanol, CO and water. Trace quantities of methane were also detected. No other products, such as higher alcohols or ethers, were found. The sum carbon selectivity of CO and methanol was always greater than 99%. The CO_2 converted always balanced with the sum of the methanol and CO produced (±7.5%) and with the water produced (±7.5%). The mass balances applied to all catalysts and no trend in the trace methane production was identified, either with Pd promotion or with deactivation (see later). Methanol and CO production were measured every hour over a period of approximately 50 h. All the catalysts deactivated with approximately 10% loss of activity in 40 h. However, from the clear trend it was possible to define initial activities and these are reported here.

The CO_2 converted to methanol as a function of synthesis gas flow rate for the various Pd-promoted catalysts is shown in Fig. 2. The two Cu/Zn/Al catalysts gave similar methanol production rates (±5%) across the range of conversions, demonstrating the reproducibility of the activity. The addition of Pd in the form of physical mixtures enhanced the CO_2 conversion to methanol. The activity amongst the physical

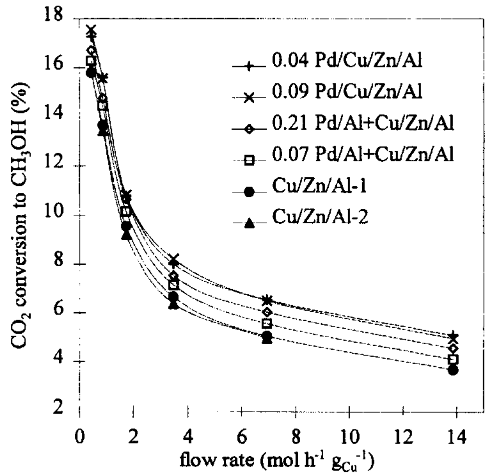

Fig. 2. Effect of Pd on methanol production from CO_2/H_2 (loadings refer to the Pd/Cu atomic ratio).

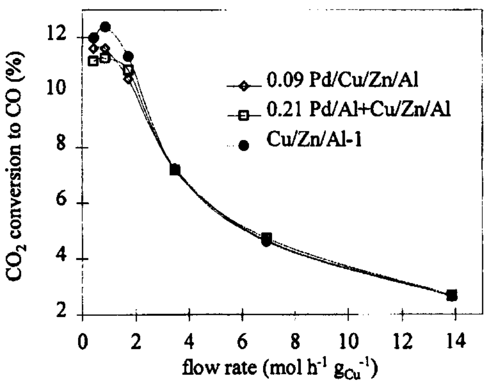

Fig. 3. Effect of Pd on CO production from CO_2/H_2 (loadings refer to the Pd/Cu atomic ratio).

mixtures increased with the higher Pd content. The activity was even greater in the case of the impregnated catalysts, although the two Pd loadings gave very similar results.

The conversions of CO_2 to CO by the reverse water-gas shift reaction are shown in Fig. 3. Only data for one Cu/Zn/Al, one Pd/Cu/Zn/Al and one Pd/Al + Cu/Zn/Al catalyst are given for clarity. Pd had no affect on CO production across the range of conversions for any of the catalysts. The reaction appears to have reached equilibrium at approximately 12% conversion at the lower flow rates, corresponding to a CO/CO_2 ratio of about 1/6.

Fig. 4 shows the observed promotion in methanol production relative to Cu/Zn/Al-1.

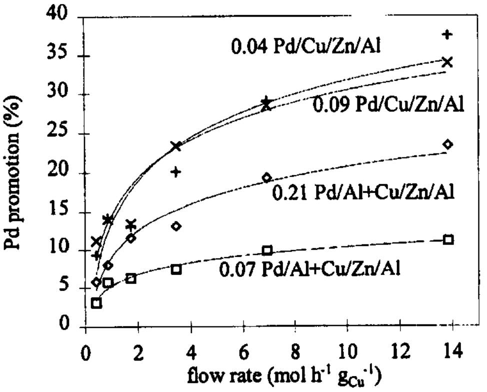

Fig. 4. Pd promotion of methanol synthesis from CO_2/H_2 (loadings refer to the Pd/Cu atomic ratio).

A promotion of approximately 35% was found for the two Pd/Cu/Zn/Al catalysts at the highest flow rate (lowest conversion). Here, the intermediate promotion of the physical mixtures is clearly seen. At the highest flow rate, the selectivity to methanol ranged from approximately 58% in the case of Cu/Zn/Al to 65% in the case of the Pd/Cu/Zn/Al catalysts. For all catalysts the extent of promotion decreased as the flow rate decreased (CO_2 conversion to methanol increased). This is consistent with the methanol reaction being closer to equilibrium (which lies at approximately 25% conversion [2]). The greater amounts of CO in the gas phase may also contribute to the loss of promotion at high conversion.

At high flow rates, the coincidence of low CO partial pressure and high Pd promotion suggests that the promotion does not involve the production of methanol from CO_2 via CO. The results are consistent with the work of Kagan et al. [13] and Chinchen et al. [14] who demonstrated the mechanism of direct CO_2 hydrogenation to methanol over Cu/Zn/Al, but contrast with the conclusion of Inui et al. [2] that methanol was produced from CO_2/H_2 via CO over Cu/Zn/Cr/Al.

The present finding that the promotion in methanol production was not dependent upon Pd loading in the impregnated Pd/Cu/Zn/Al catalysts suggests that Pd does not function as an independent catalytic site for the production of methanol in these catalysts, assuming that there was no dramatic difference in Pd dispersion between the Pd loadings. It was not possible to determine either Pd or Cu dispersions by N_2O decomposition in the impregnated catalysts [15], as noted previously for Ag/Cu systems [7]. The promotion observed over the physical mixtures in the present work supports the proposal of Inui and co-workers [1,2] and others [4] that hydrogen spillover is responsible for the increase in methanol production. The surface spillover of hydrogen from Pd would counteract the effect of CO_2 and/or water which tend to oxidise the active Cu. Rasmussen et al. [16]

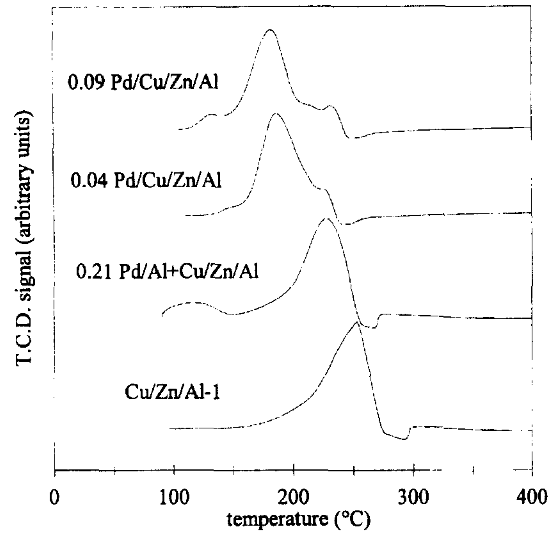

Fig. 5. TPR of calcined catalysts (loadings refer to the Pd/Cu atomic ratio).

have demonstrated recently that direct CO_2 hydrogenation to methanol over a Cu(100) single crystal occurs at a rate which is consistent with the performance of Cu/Zn/Al catalysts, with the assumption of Cu as the active site. They reported no tendency of the Cu(100) single crystal to oxidise under CO_2/H_2. Since the latter result was obtained at very low conversion, this points to water as the main source of deactivation at industrial levels of CO_2 conversion. In this context, Fujimoto and Yu [4] found that Pd promoted catalysts maintained activity for methanol synthesis from CO/H_2 when water was injected into the gas phase.

The TPR results are presented in Fig. 5. The peak reduction temperature of CuO in the calcined Cu/Zn/Al was at approximately 255°C. The addition of Pd shifted the peak reduction temperature for CuO to approximately 230°C (0.21 Pd/Al + Cu/Zn/Al), 180°C (0.04 Pd/Cu/Zn/Al) or 175°C (0.09 Pd/Cu/Zn/Al). These results show that Pd acts as a reduction promoter for CuO in the impregnated catalysts and in the physical mixtures. Interestingly, the two impregnated catalysts show very similar peak reduction temperatures consistent with the similarity of the promotion effect on the conversion of CO_2 to methanol. Furthermore, the physical mixture shows intermediate behaviour which is again consistent with the methanol synthesis activity and indicates that TPR provides a reasonable guide to the efficiency of hydrogen spillover from Pd to Cu in this catalyst system.

4. Conclusions

Activity for methanol synthesis was promoted in all Pd containing catalysts. For catalysts based on physical mixtures, the promotion in methanol synthesis was found to be intermediate and related to the Pd content. Activity was not affected by Pd loading at the higher levels of promotion achieved by impregnated catalysts. In all cases, the promotion by Pd was not related to the CO partial pressure produced by the reverse shift reaction. The results point to the promotion of CO_2 hydrogenation to methanol by hydrogen spillover from Pd to Cu. The spillover would counteract the oxidising effect of CO_2 or, more likely, water, on the basis of comparison with previously published work.

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