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Effect of CO_2 on the Conversion of H_2/CO to Methanol over Copper–Chromia Catalysts

Recently, Klier *et al.* (*1*) reported that the addition of CO_2 to the H_2/CO synthesis gas feed stream enhanced the specific rate of CH_3OH formation. The catalytic activity passed through a maximum at ~2% CO_2 [total composition 70% H_2, 30% (CO + CO_2)]. Klier *et al.* concluded this was a true promoter effect (CO_2 was neither a reactant nor a suppressor of the CO disproportionation reaction), whereby the oxidizing potential of CO_2 stabilized Cu^+ from reduction to Cu^0 in the reducing H_2/CO environment. Because CO adsorption and reduction to CH_3OH was presumed to occur on Cu^+ ions dissolved in the ZnO lattice, they stated there should be a direct relationship between the surface concentration of Cu^+ and methanol activity. Further, a maximum in CH_3OH activity was observed as the concentration of CO_2 in the feed stream was varied from 0 to 30%; this behavior was attributed to the balance between the promoting and inhibiting effects of CO_2, the latter resulting from the competitive adsorption of CO_2 and CO on catalytically active sites.

In a prior note (*2*), we reported that Cu–Cr_2O_3 was a selective CH_3OH catalyst and that the rate of CH_3OH production was directly related to the amount of stable surface Cu^+ sites, as detected by X-ray photoelectron spectroscopy (XPS). However, the effect of CO_2 on the concentration of Cu^+ sites and subsequent CH_3OH activity has not yet been explored for Cu–Cr_2O_3 catalysts. Therefore, we report here the effects of CO_2 addition to H_2/CO (synthesis gas) on CH_3OH formation and on surface Cu^+ concentration for Cu–Cr_2O_3 catalysts.

The preparation of Cu–Cr_2O_3 (Cu/Cr = 1/1) and the XPS technique (and spectra interpretation) were detailed earlier (*2*). Prior to evaluation of catalytic activity and XPS analysis, the catalyst was calcined at 350°C for 2 h in flowing air and then pretreated at 270°C for 2 h in flowing H_2 at 1 atm pressure. XPS measurements were made in a combined 1-atm reaction chamber and ultrahigh-vacuum analysis chamber.

The steady-state catalytic activities were determined in a single-pass flow reactor; differential CO conversion levels of <2% were maintained during reaction. The reaction conditions were 270°C, 750 psig overall pressure, and feed compositions of 67% H_2, 20% CO, 13% (CO_2 + He). With He as a diluent, the H_2 and CO partial pressures were kept constant as the CO_2 partial pressure was varied.

Temperature-programmed desorption (TPD) was used to examine the possibility of competitive CO_2 adsorption on CO adsorption sites. The TPD used was a dynamic one in which He at 80 (STP) ml/min was used as a sweep gas to transfer the desorbed gases from the Cu–Cr_2O_3 surface to the differentially pumped inlet system of a quadrupole mass spectrometer. Before the TPD spectra were run, CO or CO_2/CO were chemisorbed onto the H_2-reduced and vacuum-pretreated Cu–Cr_2O_3 surface at 25°C from flowing streams of CO and 5% CO_2/95% CO, respectively. Reversibly adsorbed CO and CO_2 were removed from the surface by evacuating to 10^{-2} Torr before the TPD experiments were conducted.

For Cu–Cr_2O_3 the CH_3OH activity did not increase when CO_2 was added to the syngas feed (Fig. 1). Rather, the rate of CH_3OH formation declined ~30% when

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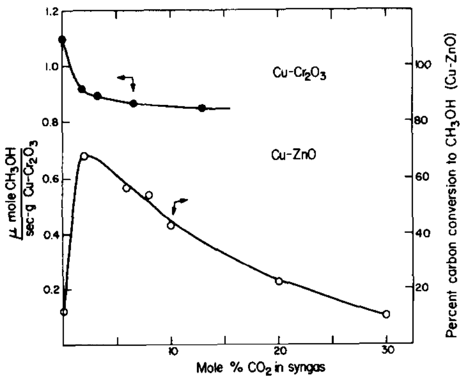

FIG. 1. The CO_2 dependency for CH_3OH formation over Cu–Cr_2O_3 and Cu–ZnO (Klier). Reaction conditions for Cu–Cr_2O_3: 750 psig, 270°C, 67% H_2, 20% CO, 13% (CO_2 + He). Reaction conditions for Cu–ZnO: 1000 psig, 250°C, 70% H_2, 30% (CO + CO_2). Selectivity to CH_3OH is greater than 93% for Cu–Cr_2O_3.

CO_2 at levels as low as 2% was added. The activity remained essentially constant as the CO_2 level was increased to 13%, suggesting a pseudo-zero-order CO_2 dependency. The results of Klier *et al.* (*1*) for Cu–ZnO (Cu/Zn = 3/7) (Fig. 1) are in contrast to those for Cu–Cr_2O_3 and reveal a maximum in activity at ~2% CO_2.

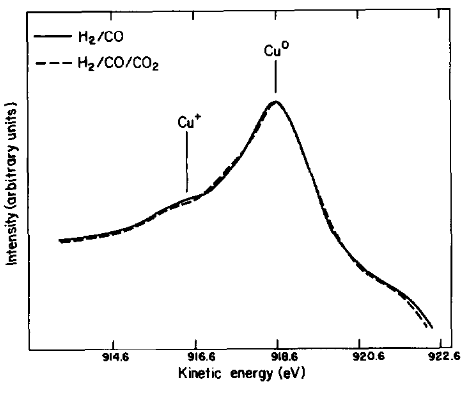

FIG. 2. Cu $L_3M_{4,5}M_{4,5}$ X-ray-induced Auger spectra for 1 : 1 Cu–Cr_2O_3 catalyst calcined in air at 350°C and heated in flowing H_2 at 1 atm and 270°C: solid line represents subsequent reaction in flowing 67% H_2/33% CO; dashed line represents reaction in flowing 67% H_2/20% CO/13% CO_2.

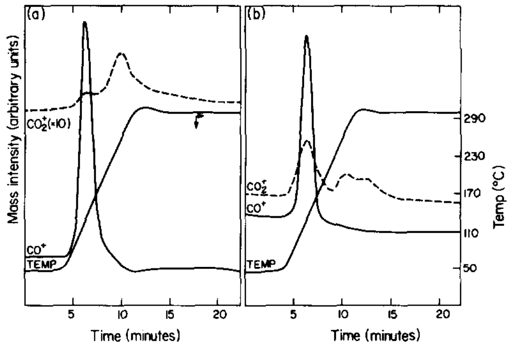

FIG. 3. Temperature-programmed desorption of CO (a) and 5% CO_2/95% CO (b) from Cu–Cr_2O_3. Note the scaling factor difference for CO_2 in (a). Mass fragmentation of CO_2 to form CO + O has been taken into account for the CO^+ peak.

The XPS results in Fig. 2 also show that the addition of CO_2 to the feed had no effect on the amount of stable Cu^+ present on the Cu–Cr_2O_3 surfaces. Given the direct relationship between CH_3OH activity and the concentration of stable surface Cu^+ sites established earlier (*2*), we would not expect an increase in CH_3OH activity for Cu–Cr_2O_3 as CO_2 is added to the feed stream.

Thus, the Cu^+ responsible for CH_3OH formation in Cu–Cr_2O_3 would appear to be more stable than the Cu^+ present in Cu–ZnO. Klier *et al.* (*1*) discuss the active Cu^+ in Cu–ZnO as being dissolved in the ZnO lattice, presumably as Cu^+ ions substitutionally and/or interstitially positioned in the ZnO lattice. The concentration of this type of Cu^+ may be sensitive to the CO/CO_2 ratio, which can alter the concentrations of lattice oxygen and oxygen vacancies in the ZnO lattice. On the other hand, Courty *et al.* (*3*) have postulated that the active Cu^+ present in Cu–Cr_2O_3-containing catalysts exists in a Cu^+-chromite phase. It would be expected that significant concentrations of Cu^+ should be more stable when Cu^+ is present as a surface compound than when Cu^+ is in a ZnO lattice, given the limited solubility of Cu^+ in the ZnO lattice (*1*).

Finally, comparison of the TPD spectra in Fig. 3a with those in Fig. 3b reveals that CO_2 is competitively adsorbed on CO adsorption sites, in agreement with the observation of Klier *et al.* (*1*) for Cu–ZnO. The addition of 5% CO_2 to CO results in a significant CO_2 desorption peak at the same temperature as for CO desorption (*T* ~135°C). Thus, CO_2 at levels as low as 5% competes favorably with CO for adsorption sites, explaining why the CH_3OH activity in Fig. 1 drops sharply for CO_2 levels as low as 2%. Additional evidence of CO-site blockage by CO_2 can be found by examining the magnitudes of the CO desorption curves in Fig. 3; the amplitude of the CO desorption curve when CO_2 is present in the feed stream is ~25% smaller than when CO_2 is not present.

The high-temperature CO_2 desorption curves centered at ~280 and 300°C most likely represent CO_2 desorption from noncatalytic sites present on Cr_2O_3 or Cr_2O_3-like surfaces, as discussed by Burwell and co-workers (*4*).

In summary, the stability of Cu^+ responsible for CH_3OH formation in $Cu–Cu_2O_3$ catalysts is independent of the presence of CO_2 in the feed stream. Catalytically, the presence of CO_2 in the syngas inhibits the rate of CH_3OH formation, owing to the noncatalytic, competitive adsorption of CO_2 on Cu^+ sites needed for CO adsorption.

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