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Carbon nanotube-promoted Co–Cu catalyst for highly efficient synthesis of higher alcohols from syngas†

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The development of a type of carbon-nanotube-promoted Co–Cu catalyst, which displays excellent performance for highly effective and selective formation of the C_{2-4}-oxygenates, especially BuOH and DME, from syngas, is reported.

The higher alcohols (C_{2-4}-alcohols) and dimethyl ether (DME) are considered as the most important species among coal-based clean synthetic fuels and chemical feedstocks.[1] These C_{2-4}-oxygenates have been confirmed to be a better and cleaner automobile fuel with high octane number, and lower emissions of NO_x, ozone, CO, and aromatic vapors.[2] Higher alcohol synthesis (HAS) on the Cu-modified Fischer–Tropsch catalysts based on Co, Fe, or Ni have been extensively studied since the late 1970s. Some pioneering work and excellent reviews[3–9] have been published on this subject. Progress in this field has considerably contributed to the growing understanding of the nature of these catalytic reaction systems. Nevertheless, the existing technology of HAS is still on a small scale. The single-pass-conversion of the feed syngas and selectivity to C_{2-4}-alcohols were both relatively low. Under the used reaction conditions, most systems produce methanol as the main product instead of C_{2-4}-alcohols.[8–11] Development of catalysts with high efficiency and selectivity to the alcohols has been one of the key objectives for R&D efforts.

On another front, multi-walled carbon-nanotubes (MWCNTs) have been drawing increasing attention[12,13] since their discovery.[14] This new form of carbon has a much higher degree of structural perfection. MWCNTs (simplified as CNTs in later text) possess several unique features, such as, highly graphitized tube-walls, nanosized channels and sp^2-C-constructed surfaces. They also display exceptionally high mechanical strength, high thermal and electrical conductivity, medium to high specific surface areas, and excellent performance for adsorption and spillover of hydrogen, which render this kind of nanostructured carbon material full of promise as novel catalyst-promoters. Here we report the development of a type of CNT-promoted Co–Cu catalyst, which is highly active for HAS from syngas. The catalysts display excellent performance for highly effective and selective formation of the C_{2+}-oxygenates, especially BuOH and DME.

CNTs were prepared following the method reported previously.[15] The freshly prepared CNTs were purified with boiling nitric acid, followed by rinsing with de-ionized water, then drying under dry nitrogen. In the purified CNTs, contents of the total carbon and the graphitized carbon were $\geqslant$99.5% and $\geqslant$90% (mass percentage), as evidenced by elemental analysis and O_2-temperature-programmed oxidation (O_2-TPO) measurements, respectively. Previous characterization studies[15,16] have shown that this type of CNT was a "Herringbone-type" CNT, with outer diameters of 10–50 nm, inner diameters at 3–5 nm, and a N_2-BET surface area at $\sim$140 m^2 g^{-1}.

A series of CNT-promoted Co–Cu catalysts, denoted as Co_iCu_j–x%(mass percentage)CNT, were prepared by the constant-pH co-precipitation method, using the homemade CNTs and nitrates of the corresponding metallic components. In a similar way, a CNT-free conventional co-precipitated Co–Cu catalyst was also prepared to be used as reference. Catalysts were then characterized through H_2-temperature-programmed reduction and desorption (H_2-TPR and H_2-TPD) tests, XRD and XPS spectroscopies.

Performance of the catalysts for the HAS from syngas was evaluated in a continuous-flow reactor-GC combination system with a pre-mixed feed gas composition of $H_2/CO/CO_2/N_2$ = 46/46/5/3 (v/v) under 523–583 K, 5.0 MPa. Prior to the reaction, the catalyst sample was pre-reduced with 5%H_2 + N_2 at 523 K for 16 h. The data were all taken 120 minutes after the reaction started and a stationary activity appeared. CO conversion was determined through an internal standard, and the carbon-based selectivity of the carbon-containing products (including alcohols, alkanes, and other oxygenates) was calculated by an internal normalization method.

We first investigated the reaction activity of HAS from syngas over a series of Co_3Cu_1–x%CNT catalysts, with the Co/Cu molar ratio fixed at 3 : 1 and varying CNT-additive level. The observed sequence of CO conversion over these catalysts is Co_3Cu_1–11.2%CNT > Co_3Cu_1–9.2%CNT $\geqslant$ Co_3Cu_1–16.0%CNT > Co_3Cu_1–0.0%CNT. The optimal mass% of the CNTs appeared to be $\sim$11%. Over the Co_3Cu_1–11.2%CNT catalyst under the reaction conditions of 573 K, 2.0 MPa, feed-gas $H_2/CO/CO_2/N_2$ = 46/46/5/3 (v/v) and GHSV = 3000 mL(STP) h^{-1} $g_{\text{cat.}}^{-1}$, the observed CO conversion reached 56.7%, while that over the other three catalysts was 54.4%, 51.7% and 40.1%, successively.

The Co/Cu molar ratio of the catalyst was then optimized. The results showed that the observed sequence of reactivity for the HAS as: Co_3Cu_1–11%CNT > Co_4Cu_1–11%CNT > Co_2Cu_1–11%CNT. Over these catalysts at the aforementioned conditions, the CO conversions were 56.7%, 52.9% and 37.7%, successively, with a Co/Cu molar ratio of 3 : 1 being optimal.

In order to evaluate the performance of the catalysts under working conditions for higher extent of reaction, the HAS reaction was conducted at higher pressure (5.0 MPa) and GHSV (10000 mL(STP) h^{-1} $g_{\text{cat.}}^{-1}$). The results showed that CO conversion observed on the Co_3Cu_1–11%CNT catalyst reached

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38.0% at 573 K, which was 1.50 times that of the CNT-free counterpart, Co_3Cu_1, under the same conditions (25.3%).

We also observed that incorporation of an appropriate amount of CNTs into the Co_3Cu_1 not only increased the catalyst activity for CO conversion significantly, but also dramatically improved its selectivity towards alcohol formation. Fig. 1 shows that the observed carbon-based selectivity for formation of $C_{1–4}$-oxygenates, $C_{1–4}$-alkanes and CO_2 was 70.5%, 28.0% and 1.4%, respectively, over the CNT-promoted Co_3Cu_1 catalyst at 573 K; while over the CNT-free Co_3Cu_1 catalyst under the same conditions, these values were 63.9%, 33.1% and 3.0%, respectively.

It should be pointed out that over the CNT-promoted Co_3Cu_1 catalyst, BuOH and DME became two dominant oxygenated products, with the carbon-based selectivity reaching 45.0% and 14.8% at 573 K, with the corresponding selectivity of PrOH, EtOH, and MeOH, merely being 5.1%, 2.7% and 1.1%, respectively. In comparison, these numbers were 22.6%, 20.1%, 9.9%, 3.4% and 7.4%, respectively, over the CNT-free counterpart, Co_3Cu_1, at the same conditions. It could be estimated from the observed selectivities of the HAS over the CNT-promoted Co_3Cu_1 catalyst that the mass% of BuOH and DME combined reaches ~83% in the total $C_{1–4}$-oxygenates obtained at 573 K, a good prospect for such oxygenated products to be used as gasoline additives or even alternative automobile fuels.

Interestingly, in contrast to the HAS systems reported previously,[8–10] the presence of a proper amount (5–6%) of CO_2 in the feed gas over the CNT-promoted Co–Cu system was found to be highly beneficial, instead of harmful, to CO conversion and selective formation of the oxygenated products, especially BuOH. The results over the Co_3Cu_1–11%CNT catalyst showed that addition of ~5% of CO_2 to the feed gas led to an increase by 40% (38.0% *vs.* 27.1%) in CO-conversion at 573 K, accompanied with a dramatic improvement in selectivity of the total oxygenates and BuOH (from 42.4% and 7.4% to 70.5% and 45.0%, respectively) and a substantial decrease in selectivity of $C_{1–4}$-alkanes and CO_2 (from 50.3% and 7.3% to 28.0% and 1.4%, respectively) (Fig. 1a *vs.* Fig. 2).

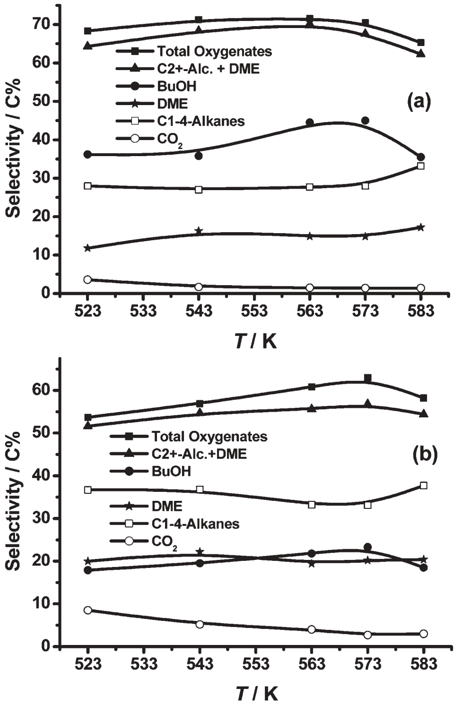

Fig. 1 Dependence of selectivity of products in the HAS upon temperature over: (a) Co_3Cu_1–11%CNT and (b) Co_3Cu_1; at 5.0 MPa, $H_2/CO/CO_2/N_2$ = 46/46/5/3 (v/v), GHSV = 10000 mL(STP) h^{-1} $g_{\text{cat.}}^{-1}$.

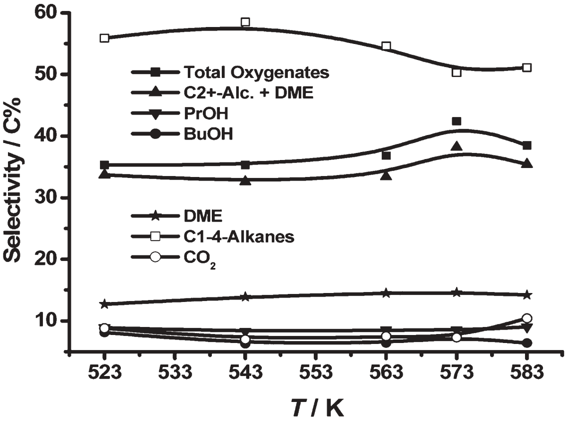

Fig. 2 Dependence of selectivity of products in the HAS upon temperature over Co_3Cu_1–11%CNT at 5.0 MPa, $H_2/CO/N_2$ = 45/45/10 (v/v), GHSV = 10000 mL(STP) h^{-1} $g_{\text{-cat.}}^{-1}$.

It was found by H_2-TPR testing that appropriate incorporation of a minor amount of CNTs into the Co_3Cu_1 led to a lowering in its reduction-temperature, simultaneously increasing the Co_xCu_y species reducible to lower valence-state(s) in the total Co_3Cu_1 amount, with a 25% increase in the specific H_2-consumed amount (*i.e.*, the amount of hydrogen consumed by reduction of unit mass of Co_3Cu_1) estimated for the Co_3Cu_1–11%CNT *vs.* its CNT-free counterpart. The XRD measurement demonstrated that, in the functioning catalysts, the Co–Cu components existed mainly in the forms of CoCu-alloy and divided metallic Cu_y^0, and that the presence of a divided metallic Co_x^0-phase could not be excluded. Moreover, the content level of either Co–Cu spinel or Co_3O_4 phase was extremely low, especially in the CNT-promoted system.

XPS measurements revealed that significant differences (Fig. 3) in the valence-state of the surface Co-species, but little difference in that of Cu (not shown), existed between the functioning Co_3Cu_1–11%CNT catalyst and its CNT-free counterpart. On the CNT-free catalyst, relatively large amounts of the surface Co-species were in the Co^0 [Co^0(2p) = 778.0 eV (B.E.)] form and minor quantities were in the CoO [Co^{2+}(2p) = 780.4 eV (B.E.)] form when fed with the CO_2-free syngas (Fig. 3c), while a dominant amount was in the CoO and a little in the Co^0 form when fed with the CO_2-containing syngas (Fig. 3a). On the CNT-promoted catalyst, in addition to Co^0 and CoO, new Co-species with the Co^{n+}(2p) at ~780.0 eV (B.E.) were observed when fed with the CO_2-free syngas (Fig. 3d); these Co-species may be ascribed to CoOOH and/or Co_3O_4.[17] It was particularly interesting that the Co^0 nearly vanished, while the CoOOH/Co_3O_4 became the predominant Co-species at the functioning surface of the CNT-promoted catalyst fed with the CO_2-containing feed syngas (Fig. 3b). It was probably such types of surface Co^{n+}-species (CoOOH/Co_3O_4) that were closely related to the highly selective formation of HAS. This result also implied that the CO_2 additive in the feed syngas played an important role in stabilizing the surface Co-species in the form of

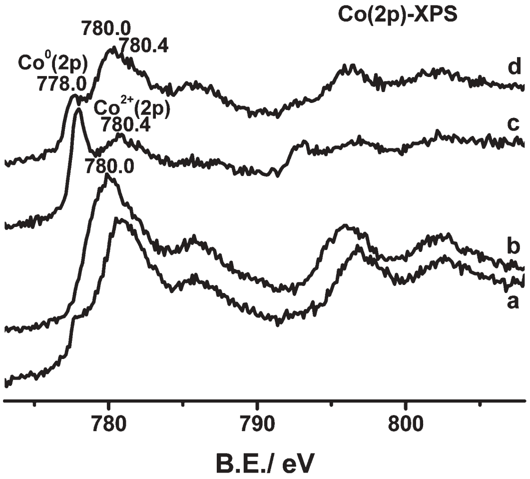

Fig. 3 Co(2p)-XPS-spectra of the functioning catalysts: (a) Co_3Cu_1 and (b) Co_3Cu_1–11%CNT, both fed with the CO_2-containing syngas: $H_2/CO/CO_2/N_2$ = 46/46/5/3 (v/v); (c) Co_3Cu_1 and (d) Co_3Cu_1–11%CNT, both fed with the CO_2-free syngas: H_2/CO//N_2 = 45/45/10 (v/v).

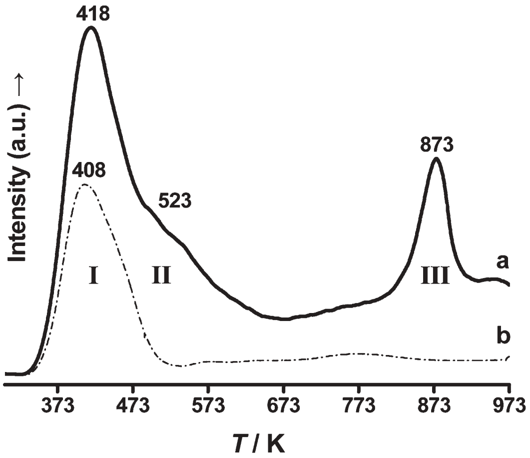

Fig. 4 H_2-TPD spectra of the pre-reduced catalysts: (a) Co_3Cu_1–11%CNT and (b) Co_3Cu_1.

CoOOH/Co_3O_4, and increasing the probability of chain termination to form oxygenated products.

It is evident that the high reactivity, especially the high specific reaction-rate and high selectivity to C_{2+}-oxygenates, for the syngas conversion over the CNT-promoted Co_3Cu_1 catalyst is closely related to the peculiar structure and properties of the CNTs. The excellent performance of the CNTs in H_2-adsorption/spillover[16,18] and electron transport is particularly important from a chemical catalysis point of view. The H_2-TPD spectra (Fig. 4) of the pre-reduced catalysts showed that, on the CNT-promoted system, the observed H_2-TPD peaks were present at 418 K (peak-I), 523 K (peak-II, a shoulder) and 873 K (peak-III). In contrast, the intensity of H_2-TPD peaks observed on the CNT-free system, Co_3Cu_1, was much lower, especially in the higher-temperature region spanning from peak-II to peak-III, with an estimated ratio of 80 : 10 for Co_3Cu_1–11%CNT : Co_3Cu_1 in their relative area-intensity of the TPD peaks in this higher-temperature region. It is conceivable that, at the temperatures for the HAS (523–583 K for the present work), the surface concentration of weakly adsorbed H-species associated with peak-I was extremely low, and most of the H-adspecies at the surface of the functioning catalyst were medium-strongly or strongly adsorbed, corresponding to peaks II and III. It was most probably those H-adspecies associated with peaks II and III that were closely associated with the HAS.

Based upon the above TPD results, it could be inferred that, under the conditions of the HAS, there existed a considerably larger amount of reversibly adsorbed H-species on the CNT-promoted catalyst, which would generate surface micro-environments with a high stationary-state concentration of H-adspecies on the catalyst. Those active H-adspecies could be readily transferred to Co_iCu_j active sites *via* CNT-promoted hydrogen spillover and thus increase the rate of a series of surface hydrogenation reactions in the HAS. This is very similar to the case of methanol synthesis from syngas over the CNT-promoted Cu–ZnO–Al_2O_3 catalysts.[18] Alternatively, incorporation of a high stationary-state concentration of H-adspecies on the surface of the catalyst with an appropriate level of CO_2 in the feed gas would effectively inhibit the water–gas shift side-reaction, which would also contribute considerably to an increase in the product yields.

In conclusion, the present work shows that the CNTs could serve as excellent catalyst-promoters. The CNT-promoted Co_iCu_j catalyst achieves highly selective formation of BuOH and DME from syngas, and demonstrates great potential in commercial use for HAS. The results also shed some light on the understanding of promoter action by the CNT additive and on the design of catalyst for the HAS.

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