Catalysis Letters Vol. 111, Nos. 3–4, November 2006 (© 2006)
DOI: 10.1007/s10562-006-0154-3

Co-decorated carbon nanotube-supported Co–Mo–K sulfide catalyst for higher alcohol synthesis

Xiao-Ming Ma, Guo-Dong Lin, and Hong-Bin Zhang*

Department of Chemistry & State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, China

Received 17 May 2006; accepted 8 August 2006

Using chemical reduction-deposition method, a type of metallic cobalt-decorated multi-walled carbon nanotubes, noted as *y*%(mass percentage)Co/MWCNTs, was prepared. TEM, SEM and XRD measurements demonstrated that the metallic cobalt was evenly coated on the MWCNT substrate, with granule-diameter of the Co_x^0-crystallites of 5–8 nm. Using the *y*%Co/MWCNTs as support, a type of supported Co–Mo–K sulfide catalysts, noted as $x\%(Co_iMo_jK_k)/(y\%Co/MWCNTs)$, for higher alcohol synthesis (HAS) was developed. It was experimentally shown that using the Co-modified MWCNTs in place of simple MWCNTs or activated carbon (AC) as the catalyst support led to a significant increase in activity of CO hydrogenation conversion and improvement in the selective formation of C_{2+}-alcohols. Under the reaction condition of 5.0 MPa, 613 K, $CO/H_2/N_2 = 45/45/10$ (v/v) and GHSV = 3600 $ml_{STP}h^{-1}\ g_{-cat.}^{-1}$, the observed STY of $C_{1–4}$-alcohols reached 154.1 $mgh^{-1}g_{-cat.}^{-1}$ at 12.6% conversion of CO over the $11.6\%(Co_1Mo_1K_{0.6})/(6.4\%Co/MWCNTs)$ catalyst, which was 1.76 and 2.33 times as high as that (87.7 and 66.1 $mgh^{-1}g_{-cat.}^{-1}$) of the reference systems supported by simple MWCNTs and AC respectively. Ethanol became the predominant product of the CO hydrogenation, with carbon-based selectivity ratio of $C_{2–4}$-alcohols to CH_3OH reaching 3.6 in the products. It was experimentally found that using the Co-modified MWCNTs in place of simple MWCNTs or AC as the catalyst support caused little change in the apparent activation energy for the conversion of CO, but led to a slight increase in the molar percentage of catalytically active Mo-species (Mo^{4+}) in the total Mo-amount at the surface of the functioning catalyst. Based upon the results of TPD investigation, it could be inferred that, under the reaction condition of HAS, there existed a considerably larger amount of adsorbed H-species and CO-species on the functioning catalyst, thus in favour of increasing the rate of a series of surface hydrogenation reactions in HAS.

KEY WORDS: Co-modified carbon nanotubes; sulphided $x\%(Co_iMo_jK_k)/(y\%Co/CNTs)$ catalyst; CO hydrogenation; higher alcohol synthesis.

1. Introduction

Multi-walled carbon-nanotubes (MWCNTs), as a novel nano-carbon support or promoter of catalysts, have drawn increased attention recently [1–3]. Catalytic applications range from selective hydrogenation of α,β-unsaturated aldehydes [4], hydrofomylation of alkenes [5], ammonia synthesis [6], Fischer–Tropsch synthesis [7], methanol and higher alcohol synthesis [8–10], to dehydrogenation of alcohols [11], oxidation [12] and electrocatalysis [13], etc. The catalytic studies conducted so far on MWCNT-based systems have shown promising results in terms of activity and selectivity. From a chemical catalysis point of view, the excellent performance of MWCNTs in adsorption-activation of hydrogen and in promoting spillover of adsorbed H-species is very attractive, in addition to its high mechanical strength, nanosize channel, sp^2-C constructed surface, graphite-like tube-wall and high thermal/electrical conductivity; while modification of some transition-metals to MWCNTs might result in the further enhancement of their performance in adsorbing and activating hydrogen, as well as promoting H-adspecies spillover.

How to deposit and evenly disperse metals or metal compounds onto MWCNT surface is one of the key technical problems for preparation of MWCNT-based functionalized materials. The most straightforward route reported previously was to melt the element on MWCNT surface [14]. However, research efforts by Ebbesen [15] showed that only liquids with low surface tensions could wet MWCNT surface. Ang *et al.* [16] reported a so-called “two-step sensitization-activation method”, in which the surface of oxidized MWCNTs was further activated by the introduction of catalytic nuclei, and then the activated MWCNTs catalyze metal deposition specifically onto their surface upon immersion in electroless plating baths. Metal decorated-MWCNTs could also be prepared by metal vapor deposition. Nevertheless, the dispersion of metal or metal compounds on MWCNTs by chemical means is still largely based on conventional catalyst preparation techniques, such as wet impregnation followed by chemical reduction [17].

---

*To whom correspondence should be addressed.
E-mail: hbzhang@xmu.edu.cn

1011-372X/06/1100–0141/0 © 2006 Springer Science+Business Media, Inc.

Higher alcohol synthesis (simplified as HAS in later text) on MoS_2-based catalysts has been extensively studied since the mid-1980s. A number of pioneer works and excellent reviews [18–23] 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+}-alcohols both were relatively low. Under the used reaction conditions, most systems produce methanol as the main product instead of C_{2+}-alcohols [23–26]. Development of catalysts with high efficiency and selectivity to C_{2+}-alcohols has been one of the key objectives for R&D efforts.

In the present work, a metal cobalt-decorated multi-walled carbon nanotubes, noted as y%(mass percentage)Co/MWCNTs, was prepared by chemical reduction-deposition, and characterized through TEM/EDX, SEM, XRD and H_2(or CO)-TPD (temperature-programmed desorption) measurements. Using the cobalt-decorated MWCNTs as support, a type of sulphided Co–Mo–K catalysts supported by the y%Co/MWCNTs was developed. The catalysts displayed higher catalytic activity and selectivity for HAS from syngas, as compared to the reference catalyst supported by the simple MWCNTs or AC (a conventional activated carbon).

2. Experimental

2.1. Preparation of MWCNTs

The MWCNTs were synthesized by the catalytic method reported previously [27]. The prepared MWCNTs were a herringbone-type of multi-walled carbon nanotubes, with the outer diameters of 10–50 nm, inner diameters at 3–5 nm, and N_2-BET surface area at ~140 m^2g^{-1}. The freshly prepared MWCNTs were purified with boiling concentrated nitric acid, followed by rinsing with de-ionized water, then drying under dry nitrogen. Open-end MWCNTs with oxidized surface were thus obtained. In the purified MWCNTs, contents of the total carbon and the graphitized carbon were ≥99.5% and ≥90% (mass percentage), as evidenced by elemental analysis and O_2-TPO (temperature-programmed oxidation) measurements, respectively.

2.2. Preparation of Co-decorated MWCNTs

Referring to the method used by Ang *et al.* [16], Co-decorated MWCNTs were prepared in the following procedure. About 3.0 g of the purified MWCNTs was put into a Pyrex flask containing 50 ml of 0.1 M buffer solution of $SnCl_2$–HCl, followed by ultrasonating for 3 min, subsequently agitating for 7 min. The mixture was separated by centrifugation. The obtained sensitized MWCNTs was rinsed with de-ionized water, and then was put into a Pyrex flask containing 50 ml of 0.0028 M buffer solution of $PdCl_2$–HC1, followed by agitating for 30 min, subsequently centrifugation-separating and rinsing. The obtained activated MWCNTs were dried, and then put into a $Co(OAc)_2$-ethylenediamine complexes solution, which had been prepared previously by adding 5.0 ml of aqueous solution containing 1.27 g of $Co(OAc)_2$ (of AR grade) drop-wise into 10 ml of ethylenediamine (of AR grade) under vigorous stirring. The mixture was continuously stirred for ~5 min, followed by adding drop-wise 5.0 ml of aqueous solution containing 3.2 g NaOH and 1.0 g $NaBH_4$ under vigorous stirring. With pH adjusted at ~12, the precipitate was continuously stirred at 393 K till no more bubble generated, followed by aging overnight at room temperature, and then filtering. It was then rinsed several times with deionized water, finally dried at 373 K, and a Co-decorated MWCNT material was thus obtained. Element analysis showed that cobalt content in the prepared material was at 6.4% (mass percentage), symbolized as 6.4%Co/MWCNTs. By changing loading-amounts of MWCNTs, $Co(OAc)_2$ and the additives, a series of y%Co/MWCNTs with varying Co contents could be prepared.

2.3. Preparation of supported Co–Mo–K catalysts

Supported Co–Mo–K catalysts were prepared by the conventional incipient wetness method, with the Co-decorated MWCNTs, the simple MWCNTs and AC as carrier, respectively. The Co-decorated MWCNT supported Co–Mo–K catalysts was prepared by impregnating a certain amount of y%Co/MWCNTs with potassium carbonate aqueous solution containing a calculated amount of K, followed by drying and calcining at 573 K under N_2 atmosphere for 2 h; and then, an aqueous solution containing a calculated amount of $(NH_4)_6Mo_7O_{24}\ 4H_2O$ was impregnated onto the above K-impregnated intermediate, followed by drying; and finally, an aqueous solution containing a calculated amount of $Co(NO_3)_2$ was impregnated onto the above K and Mo impregnated intermediate, followed by drying at 393 K for 12 h and calcining at 673 K for 24 h under N_2 atmosphere, thus yielding the oxidized precursor of y%Co/MWCNTs supported Co–Mo–K catalyst, symbolized as $x\%(Co_iMo_jK_k)/(y\%Co/MWCNTs)$. The reference catalysts supported by the MWCNTs and the AC, noted as $x\%(Co_iMo_jK_k)$/MWCNTs and $x\%(Co_iMo_jK_k)$/AC, respectively, were prepared in the similar way. Prior to being impregnated, the AC support (Shanghai Chem. Reagent Co., with 650 m^2g^{-1} of N_2-BET-SSA) was pretreated first with 10% NaOH aqueous solution and then with 30% HNO_3 solution, followed by rinsing with de-ionized water and drying at 383 K for 12 h. All samples of oxidized catalyst-precursors were pressed, crushed, and sieved to a size of 40–80 mesh for the activity evaluation.

2.4. Catalyst evaluation

The y%Co/MWCNTs supported Co–Mo–K catalysts were tested for HAS, and compared with the reference systems supported by simple MWCNTs and AC. 0.80 g of catalyst sample was used for each test. Prior to the reaction, the oxidized catalyst-precursor was *in-situ* pre-reduced/sulphided in a H_2-carried 5v%CS_2 gaseous mixture stream at 0.1 MPa and 1800 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$. The sulphidation temperature was programmedly raised from room temperature to 673 K and kept at 673 K for 6 h, and then lowered down to desired temperature for the catalyst test. The HAS from syngas over the catalysts was conducted in a continuous-flow micro-reactor-GC combination system at a stationary state with pre-mixed feed-gas composition of $H_2/CO/N_2 = 45/45/10$ (v/v) under 573–623 K, 2.0–5.0 MPa. The reactants and products were determined by an on-line GC (Model GC-950) equipped with dual detectors (TCD and FID) and dual columns filled with carbon molecular sieve (TDX-01) and 5%Carbowax 20M/Carbopack B, respectively. The former column (3.0 m length) was used for the analysis of N_2 (as internal standard), CO, CH_4 and CO_2, and the latter (60 cm length) for C_{1-4}-alkanes, C_{1-4}-alcohols and other oxygenates. The data were all taken 120 min after the reaction started, since when a stationary stage of 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.

2.5. Characterization of the MWCNT-based supports and catalysts

Specific surface area (SSA) was determined by N_2 adsorption using a Micromeritics Tristar-3000 (Carlo Erba) system. TEM/EDX and SEM observations were performed by FEI-F30 and LEO-1530 electron microscopes respectively. XRD measurements were carried out on a Rigaku D/Max-C X-ray Diffractometer with Cu–Kα radiation at a scanning rate of 8° min^{-1}. XPS measurements were done on a Quantum 2000 machine with Al–Kα radiation (15 kV, 25 W, $h\nu = 1486.6$ eV) under UHV (10^7 Pa), calibrated internally by the carbon deposit C(1s) B. E. at 284.6 eV.

The comparative investigation of adsorption of H_2 on the 6.4%Co/MWCNTs, simple MWCNTs and AC, as well as the catalysts supported by these support-materials, was conducted by using H_2-temperature-programmed desorption (TPD) method on a home-made adsorption-desorption/reaction system. About 50 mg of sample was used for each test. Prior to TPD measurement, the sample was treated *in-situ* in the TPD equipment by a N_2-carried 5 v% H_2 gaseous mixture stream at 573 K for 12 h and then flushed by an Ar (of 99.999% purity) stream at 573 K for 30 min to clean its surface, followed by cooling down to 433 K, switching to a H_2 (of 99.999% purity) stream for hydrogen adsorption at 433 K for 60 min and subsequently at room temperature for 120 min, and then flushing by the Ar stream at room temperature till the stable baseline of GC appeared. The rate of temperature increase was 5 K min^{-1}. Change of hydrogen-signal was monitored using an on-line GC (Shimadzu GC-8A) with a TC detector. For the CO-TPD measurement, the procedure of getting sample ready and the condition of measurement were in the manner similar to that mentioned above.

3. Results and discussion

3.1. Characterization of the prepared y%Co/MWCNTs support material

The morphology, metal-particle size-distribution and surface element-composition of the prepared Co/MWCNTs nanocomposites were observed by TEM/EDX (FEI-F30) and SEM (LEO-1530). The results (figure 1) showed that Co nanoparticles were quite uniform in shape and size and well distributed on the MWCNT surface. It could be estimated from figure 1(a) that the Co-particle diameters were in range of 4–7 nm. Carbon and cobalt were the predominant two elements, with the content at 82.94 atomic% and 7.23 atomic% respectively, and surface-contents of Pd and B both were under detection limit by the EDX (see Table 1).

Figure 2 displayed the XRD patterns of the simple MWCNTs and the Co-decorated MWCNTs with different Co-decorating amounts. The observed XRD peaks for these systems at $2\theta = 26.1°$, 43.1° and 53.5° were due to the reflections of (002), (100) and (004) faces of the MWCNTs, respectively [28]. The weak but distinguishable features at $2\theta = 33.4°$, 38.0° and 59.9° appeared only in the XRD patterns of the Co-decorated MWCNTs. They could be ascribed to contribution frog crystallite phase of metallic cobalt. Using the well-known Scherrer's equation [29], the estimation of particle size of metallic cobalt was made for these Co-decorated samples. The estimated particle size of metallic cobalt was ~6.8 nm for the 6.4%Co/MWCNTs, which is very close to that observed from the above TEM image; while for the samples with the Co-decorating amount at 4.0%, 4.8%, 9.9%, and 11.8%, these values were 5.2, 6.2, 7.6, and 8.4 nm, successively, showing an upward tendency of the particle size of metallic cobalt with increasing Co-decorating amounts.

3.2. Performance of sulphided Co–Mo–K catalyst supported by y%Co/MWCNTs for HAS

Our previous investigation [30] showed that among a series of sulphided MWCNT-supported $Co_iMo_jK_k$

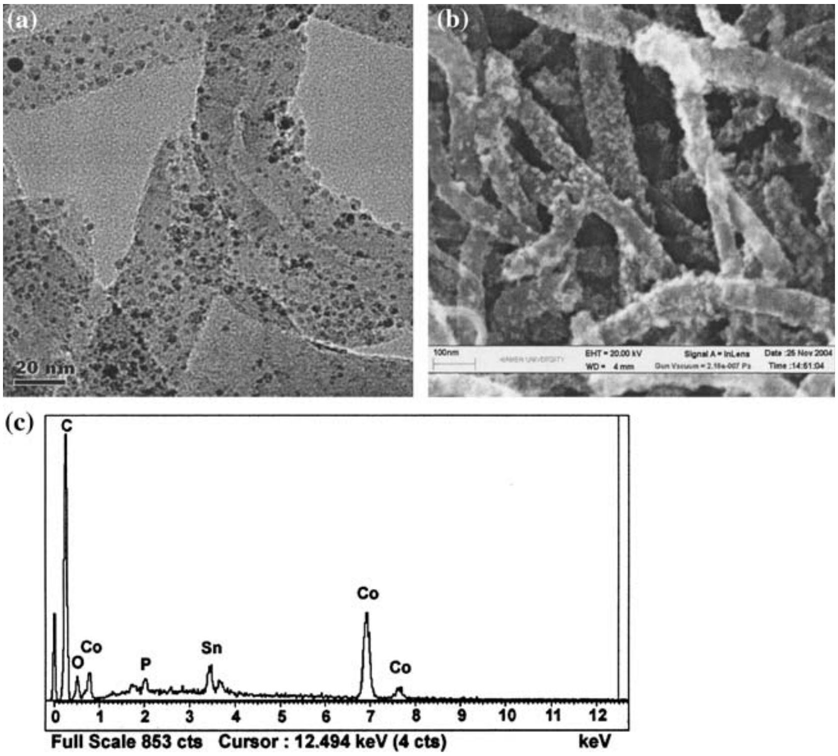

Figure 1. TEM (a) and SEM (b) images of 6.4%Co/MWCNTs with the corresponding EDX pattern (c).

catalysts, the catalyst with the composition of 11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs displayed the highest catalytic activity for HAS from syngas. In the present work, with the composition and loading amounts of the $Co_iMo_jK_k$ remained unchanged and using the Co-decorated MWCNTs in place of the simple MWCNTs as the catalyst support, the effect of modification of cobalt to MWCNT-support on performance of the corresponding catalyst for HAS was investigated. The results (in figure 3) showed that on all six catalysts supported by the *y*%Co/MWCNTs with the varying Co-decorating amounts, CO conversion (X_{CO}) fiist went up with increasing Co-decorating amount, reached a maximal at ~6.4%Co, and then went down as Co-decorating amount increased further. The sequence of these catalysts in their activity of catalyzing HAS is: 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) > 11.6% ($Co_1Mo_1K_{0.6}$)/(4.8%Co/MWCNTs) > 11.6%($Co_1Mo_1K_{0.6}$)/(9.9%Co/MWCNTs) > 1.6%($Co_1Mo_1K_{0.6}$)/(4.0% Co/MWCNTs) > 11.6%($Co_1Mo_1K_{0.6}$)/(11.8%Co/MWCNTs) ≈ 11.6%($Co_1Mo_1K_{0.6}$)/(0%Co/MWCNTs), with Co-decorating amount at 6.4% (mass percentage) being the optimal. Over the 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst under the reaction condition of 2.0 MPa, 593 K, $H_2/CO/N_2 = 45/45/10$ (v/v), GHSV = 2400 $ml_{STP}h^{-1}g_{-cat}{}^{-1}$, the yield (defined as: "*product of CO conversion and C-based selectivity*") of total alcohols reached 9.2%, while over the other five catalysts, this value was 7.8%, 7.7%, 3.4%, 2.9% and 2.9%, successively, at the same condition.

Table 1
Element composition at the surface of 6.4%Co/MWCNTs by EDX analysis

Element	C	O	P	Co	Sn	Totals
Weight%	59.49	8.11	0.90	25.43	6.08	100.00
Atomic%	82.94	8.49	0.48	7.23	0.86	100.00

In order to evaluate the performance of the catalysts under working condition with higher extent of reaction, the HAS reaction from syngas was conducted at higher pressure and GHSV. The results are shown in figure 4. Conversion of CO over the 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst increased with increasing reaction temperature, simultaneously with slowly descending the selectivity of the total alcohols and correspondingly enhancing the selectivity of the total hydrocarbons. In order to obtain high space-time-yield (STY) of alcohols, 613 K was taken as the optimal operating temperature. Under the reaction conditions of 5.0 MPa, 613 K, $CO/H_2/N_2 = 45/45/10$ (v/v), and GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$, the observed conversion of CO reached 12.6%, and the selectivities of total (i.e. C_{1-4}) alcohols, C_{1-3}-hydrocarbons and CO_2 were 70.5, 24.3 and 5.2 C%, respectively, with the corresponding STY at 154.1, 35.5 and 21.1 mg $h^{-1}g_{-cat.}{}^{-1}$, successively. Ethanol became the predominant product of the CO hydrogenation, with carbon-based selectivity ratio of $C_{2\text{-}4}$-alcohols to CH_3OH reaching 3.6 in the products. Figure 5 shows the operation stability of the

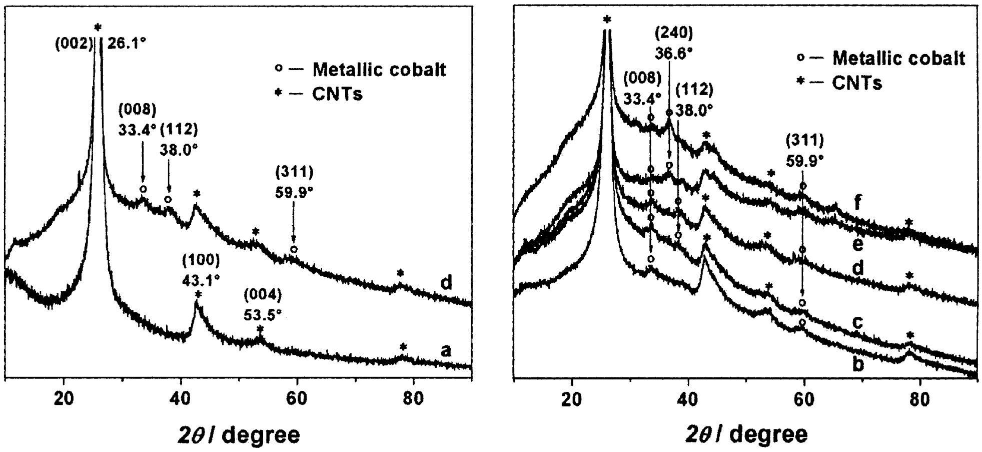

Figure 2. XRD patterns of: (a) MWCNTs; (b) 4.0%Co/MWCNTs; (c) 4.8%Co/MWCNTs; (d) 6.4%Co/MWCNTs; (e) 9.9%Co/MWCNTs; (f) 11.8%Co/MWCNTs.

6.4%Co/MWCNTs supported catalyst for HAS lasting 100 h under reaction conditions of 5.0 MPa, 613 K, $H_2/CO//N_2$ = 45/45/10 (v/v) and GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$, without obvious deactivation of the catalyst observed.

In order to gain a clear idea of the nature of promoting action by the Co-modified MWCNTs, a reference Co–Mo–K catalyst supported by the AC with the optimized composition of 50.3%($Co_1Mo_1K_{0.8}$)/AC was prepared in the similar way, and the performance of its catalyzing the HAS reaction was evaluated. The result was shown in figure 6. Under the same reaction condition of 5.0 MPa and 613 K, the observed conversion of CO and selectivity of the total alcohols reached 9.0%, and 41.3 C%, respectively, with the corresponding STY of the total alcohols at 66.1 mg $h^{-1}g_{-cat.}{}^{-1}$, which was merely 43% of that (154.1 mg $h^{-1}g_{-cat.}{}^{-1}$) of the 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst.

The results of activity evaluation of the HAS over the above catalysts supported by the three supports (6.4%Co/MWCNTs, MWCNTs and AC) were summarized in Tables 2 & 3. Table 2 also listed the result of "blank" catalytic measurement with 6.4%Co/MWCNTs support, from which it could be demonstrated that the conversion activity of CO over the Co-decorated MWCNTs was quite low under the reaction condition for HAS, with C_{1-3}-hydrocarbons as the predominant product, suggesting that this support material has little direct contribution to the formation of higher alcohols in the present work.

The above results indicated that the proper modification of a small amount of Co to the MWCNT-support led to not only significantly increasing the catalyst activity for CO conversion, but also dramatically improving the selectivity of the HAS and inhibiting the formation of CO_2 by-product. Over the 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst, the STY of C_{2-4}-alcohols achieved 108.9 mg h^{-1} $g_{-cat.}{}^{-1}$, which was 2.58 times that (42.2 mg $h^{-1}g_{-cat.}{}^{-1}$) of the counterpart supported by the simple MWCNTs and

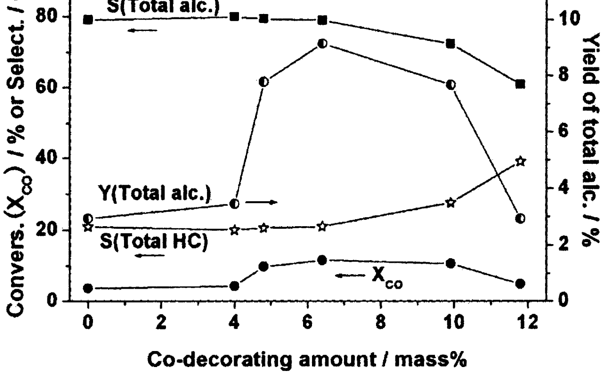

Figure 3. HAS reactivity over the 11.6%($Co_1Mo_1K_{0.6}$)/(y%Co/MWCNTs) catalysts with varying Co-decorating amounts; at: 2.0 MPa, 593 K, $CO/H_2/N_2$ = 45/45/10 (v/v), GHSV = 2400 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$.

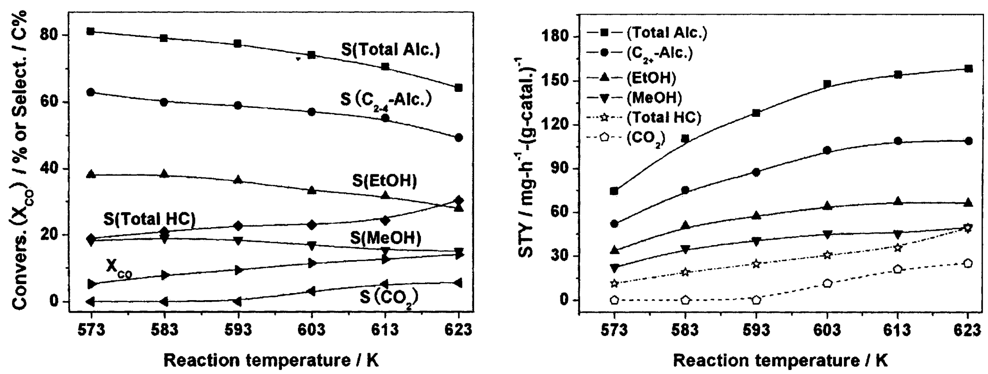

Figure 4. HAS reactivity over the sulphided 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst at varying temperatures; at: 5.0 MPa, CO/H_2/N_2 = 45/45/10 (v/v), and GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}^{-1}$.

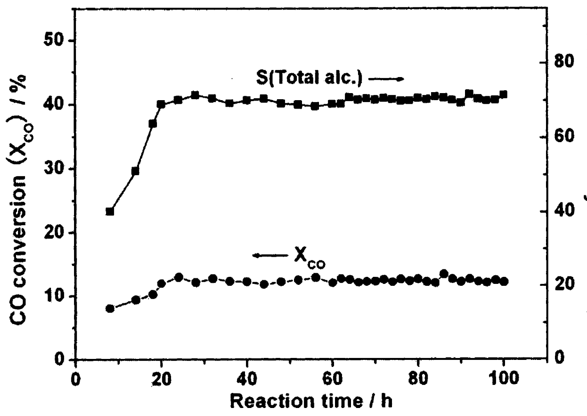

Figure 5. Operation stability of HAS lasting 100 hours over the sulphided catalyst of 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs); at: 5.0 MPa, 613 K, CO/H_2/N_2 = 45/45/10 (v/v), GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}^{-1}$.

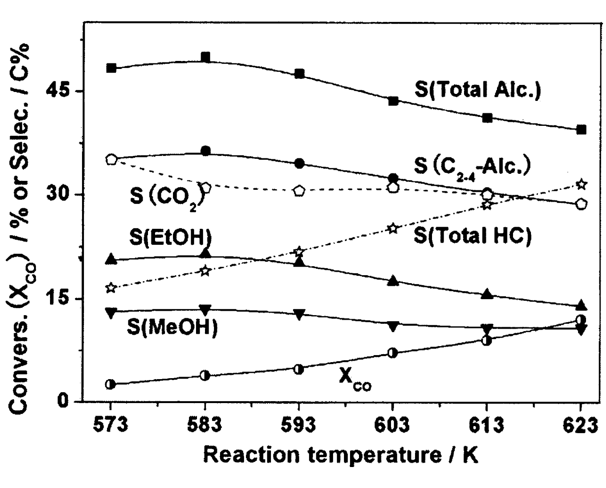

Figure 6. HAS reactivity over the sulphided 50.3%($Co_1Mo_1K_{0.8}$)/AC catalyst at varying temperatures; at: 5.0 MPa, CO/H_2/N_2 = 45/45/10 (v/v), GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}^{-1}$.

2.52 times that (43.1 mg $h^{-1}g_{-cat.}^{-1}$) of the reference catalyst supported by AC.

The apparent activation energy (E_a) of HAS reaction on these catalysts was measured under the reaction condition of 2.0 MPa, 573–623 K, H_2/CO/N_2 = 45:45:10 (v/v), GHSV = 4800 $ml_{STP}h^{-1}g_{-cat.}^{-1}$, with mass transfer limitation ruled out and the CO percent-conversion setting in the range of 1.4–10.7%, The result was shown in figure 7. The E_a observed on the 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) catalyst was 22.7 kJ mol^{-1}. This value was very close to 24.5 and 25.2 kJ mol^{-1} on the reference systems supported by MWCNTs and AC respectively. This indicated that using the Co-decorated MWCNTs in place of simple MWCNTs or AC as support of the catalyst caused little change in the apparent activation energy for HAS reaction, most likely implying that the use of Co-decorated MWCNTs in place of simple MWCNTs or AC as support did not alter the main reaction pathway of CO hydrogenation.

3.3. Post-analysis of the tested catalysts by XRD and XPS

The XRD post-analysis of the tested catalysts demonstrated that, in the tested Co–Mo–S catalysts supported by 6.4%Co/MWCNTs, simple MWCNTs and AC, the Co–Mo components existed mainly in the forms of Co–Mo–S composite species, probably including $Co_{1.62}Mo_6S_8$ and $CoMoS_{3.13}$ (with the observed XRD features at 2θ = 29.8° and 30.7°, respectively) [31], and that the presence of divided Metallic CO_x^0-phase could not be excluded, and moreover, the content level of MoS_2 phase was extremely low.

XPS measurements provide information about Co and Mo species at the surface of the tested Co–Mo–S catalysts supported by Co/MWCNTs, MWCNTs and AC respectively. There was little difference between the three catalysts in the position and shape of their Co(2p)-XPS peaks. The Co($2p_{3/2}$, $2p_{1/2}$)-XPS peaks exhibited at 779.0 and 795 eV (B. E.), with their area-intensity ratio

Table 2
Reactivity of the HAS over the sulphided Co–Mo–K catalysts supported by the Co/MWCNTs, MWCNTs AC, respectively, and over the support of Co-decorated MWCNTs

Catalyst composition optimized	CO conv./%	Selectivity / C%						
		C_{1-4}-alc.	C_{1-3}-HC	CO_2	MeOH	EtOH	PrOH	BuOH
11.6%($Co_1Mo_1K_{0.6}$)/ (6.4%Co/MWCNTs)	12.6	70.5	24.3	5.2	15.3	31.6	12.9	10.7
11.6%($Co_1Mo_1K_{0.6}$)/ MWCNTs	6.9	65.2	25.6	9.2	28.0	29.0	7.9	0.3
50.3%($Co_1Mo_1K_{0.8}$)/ AC	9.0	41.3	28.7	30.0	10.9	15.6	10.7	4.1
Blank test of support								
		Total Oxy.	C_{1-3}-HC	CO_2	MeOH	CH_4	C_2H_6	C_3H_8
6.4%Co/MWCNTs	1.65	14.4	85.6	0	14.4	56.0	15.2	14.4

Reaction condition: 5.0 MPa, 613 K, $H_2/CO/N_2 = 45/45/10$ (v/v), GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$.

Table 3
STY of the HAS over the sulphided Co–Mo–K catalysts supported by the Co/MWCNTs, MWCNTs and AC, respectively*

Catalyst composition optimized	Specific reaction activity**	STY/mg $h^{-1}g_{-cat.}{}^{-1}$						
		C_{1-4}-alc.	C_{1-3}-HC	CO_2	MeOH	EtOH	PrOH	BuOH
11.6%($Co_1Mo_1K_{0.6}$)/ (6.4%Co/MWCNTs)	78.53	154.1	35.5	21.1	45.2	66.8	23.8	18.3
11.6%($Co_1Mo_1K_{0.6}$)/ MWCNTs	43.02	87.7	20.3	20.6	45.5	33.9	8.1	0.2
50.3%($Co_1Mo_1K_{0.8}$)/ AC	12.94	66.1	29.8	87.7	23.0	23.8	14.2	5.0

* Reaction condition: 5.0 MPa, 613 K, $H_2/CO/N_2 = 45/45/10$ (v/v), GHSV = 3600 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$.

** Specific reaction activity at: mmol-CO s^{-1}[g-($Mo_1Co_1K_{0.6 \text{ ro } 8}$)]$^{-1}$.

of I(779.0) to I(795.0) being about 2. These values are characteristics of the Co sulfide species interacting with Mo species to form Co–Mo–S composite species [32]. Different from the case of Co(2p)-XPS spectra, certain difference existed between the three catalysts in the position and shape as well as relative intensity of the features associated with the Mo-species (figure 9). With reference to ref. [33] and assuming: E_b(Mo $3d_{3/2}$)-E_b(Mo $3d_{5/2}$) = 3.1 eV (B. E.) and I(Mo $3d_{5/2}$)/I(Mo $3d_{3/2}$) (intensity ratio of the peaks) = 1.5 for each kind of the Mo^{n+} species in the same valence-state, analysis and fitting of the Mo(3d)-XPS spectra of these catalysts were done. The results (figure 9 and Table 4) showed that the molar percentage of Mo^{4+}-species in the total Mo-amount at the surface of the tested catalyst of 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs) reached 79.4 mol%. This value was 1.05 times that (75.5%) of the MWCNTs-supported counterpart, and 1.17 times that (67.5%) of the AC-supported reference system. This suggested that using the Co-decorated MWCNTs in place of the simple MWCNTs or AC as support of the catalyst led to a slight increase in relative concentration of catalytically active Mo-species (Mo^{4+}) at the surface of the functioning catalyst.

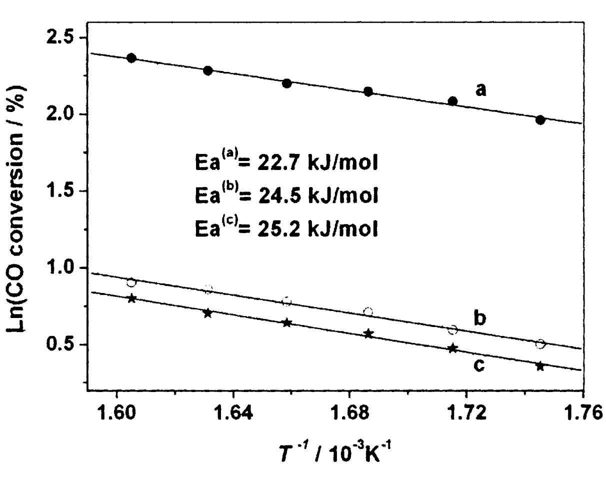

Figure 7. Arrhenius plots of HAS over the sulphided catalysts: (a) 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs); (b) 11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs; (c) 50.3%($Co_1Mo_1K_{0.8}$)/AC; at: 2.0 MPa, 563~623 K, $H_2/CO/N_2$ = 45:45:10 (v/v), GHSV = 4800 $ml_{STP}h^{-1}g_{-cat.}{}^{-1}$.

3.4. H_2(or CO)-TPD characterization of the supports and the pre-reduced/sulphided catalysts

In recent years there has been considerable experimental and theoretical interest in the use of nanostructured carbon materials as potential hydrogen sorbents. It was demonstrated by Ishikawa *et al.* [34] that graphitized carbon black surfaces were capable of rapidly equilibrating hydrogen/deuterium mixture. A dissociation rate of 2.5 × 10^{17} molecules s^{-1} (m^2-ASA)$^{-1}$ (ASA–active surface area) was measured at ambient temperatures and pressures, irrespective of the nature of the carbon material under investigation. The ASA was

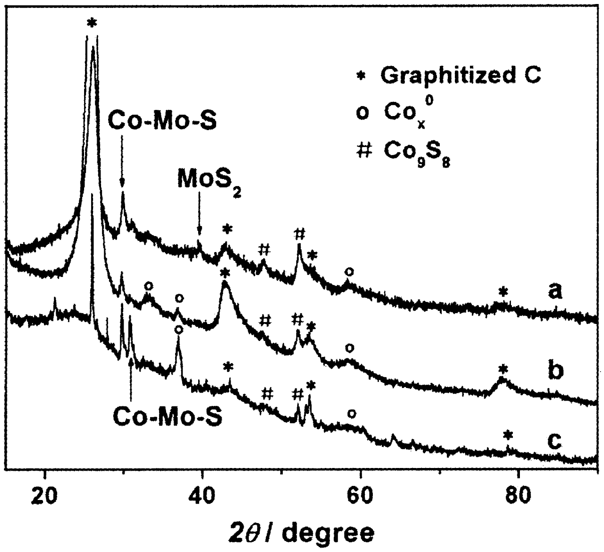

Figure 8. XRD patterns of the tested catalysts: (a) 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs; (b) 11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs; (c) 50.3%($Co_1Mo_1K_{0.8}$)/AC.

described in terms of atoms located at edge positions on the graphite basal plane and was determined from the amount of oxygen able to chemisorb at these sites. Our previous H_2-TPD investigation [35] showed that hydrogen adsorption on the MWCNTs can occur at room temperature and atmospheric pressure and that the desorbed product was almost exclusively gaseous hydrogen at temperatures lower than ~723 K, and included CH_4, C_2H_4 and C_2H_2, in addition to H_2, at temperatures of 773 K and above, which resulted from the hydrogenation of some surface carbon by H-adspecies. This implies that H_2 adsorption on the MWCNTs may be in the two forms: associative (molecular state) and dissociative (atomic state). This has also been demonstrated by our laser Raman spectroscopy (LRS) characterization of H_2/MWCNTs adsorption system [28].

The TPD profiles of H_2 and CO are shown in figure 10. Figure 10(1) showed the TPD profiles of H_2 adsorbed at 433 K followed by cooling down to room temperature on the 6.4%Co/MWCNTs, and the two reference support materials, MWCNTs and AC, respectively. It can be seen, through comparison of figure 10(1a) with figure 10(1b), that the modification of metallic cobalt to the MWCNTs resulted in a significant increase in its capacity of adsorbing hydrogen, especially the dissociatively adsorbing hydrogen H(a). Considering that the hydrogenation of some surface carbon by H-adspecies (which would lead to consumption of part of H-adspecies and formation of C_{1-2}-hydrocarbons) could occur at temperatures of 773 K and above [28, 35], we could estimate the relative area-intensities of these H_2-TPD profiles in the region of 293–723 K. Their ratio obtained was: $S_{6.4\%Co/MWCNTs}/S_{MWCNTs}/S_{AC} = 100/45/38$, indicating that the modification of the metallic cobalt to the MWCNTs led to a 1.2 times increase in its hydrogen-adsorbing capacity in the temperature range of 293–723 K. This was also 1.6 times higher than that of the AC (figure 10(1c)) under the same conditions.

As shown in figure 10(2), the CO-TPD profiles of the two MWCNT-based samples, 6.4%Co/MWCNTs and simple MWCNTs, were similar to each other in the

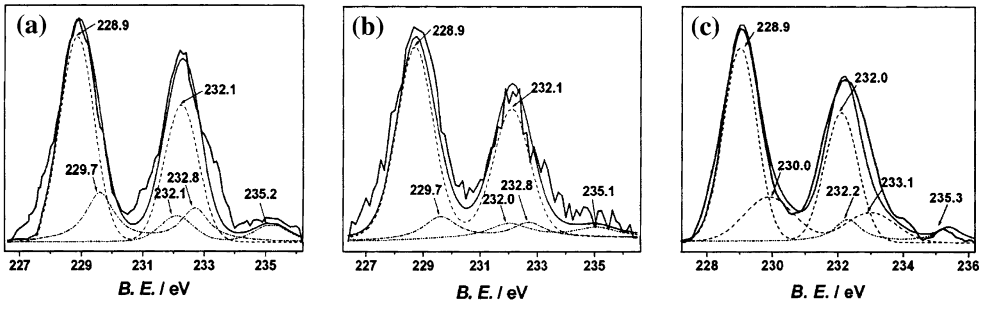

Figure 9. Mo(3d)-XPS spectra of the tested catalysts: (a) 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs); (b) 11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs; (c) 50.3%($Co_1Mo_1K_{0.8}$)/AC.

Table 4
XPS binding energies and relative contents of the Mo^{n+}-species with different valence states at the surface of tested catalysts

Catalyst sample	B. E. of $Mo(3d_{5/2})$/eV			Relative content/mol%		
	Mo^{4+}	Mo^{5+}	Mo^{6+}	Mo^{4+}	Mo^{5+}	Mo^{6+}
11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs)	228.9	229.7	232.0	79.4	13.1	7.5
11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs	228.9	229.7	232.0	75.5	14.2	10.3
50.3%($Co_1Mo_1K_{0.8}$)/AC	228.9	230.0	232.2	67.5	20.0	12.5

position and shape of their CO-TPD peaks. This could be rationalized in association with the aforementioned results of EDX measurement (see figure 1(c) and Table 1), which revealed that the principal part of the exposed atoms at the surface of 6.4%Co/MWCNTs were still sp^2-C (with the atomic% of carbon reaching 82.9%). The observed CO-TPD peaks at lower temperatures (373/348 K) were due to desorption of CO-species adsorbed weakly, while the peaks at higher temperatures (553/573 K) could be ascribed to desorption of CO-species chemisorbed strongly. Although the atomic% of cobalt at the exposed surface of 6.4%Co/MWCNTs was merely 7.2%, its modification to the MWCNTs led to a significant increase in the capacity of adsorbing CO, especially strongly chemisorbing CO. As shown in figure 10(2c), the CO-TPD profile of the AC was very different from those of the two MWCNT-based samples in the position and shape of the CO-TPD peaks. This was perhaps due to the considerable difference between the AC and the MWCNT-based materials in their structure/texture and surface properties. The relative area-intensity ratio of these CO-TPD profiles in the region of 293–673 K were estimated to be: $S_{6.4\%Co/MWCNTs}/S_{MWCNTs}/S_{AC}$ = 100/66/50, indicating that the modification of the metallic cobalt to the MWCNTs led to a 51% increase in its CO-adsorbing capacity in the above temperature range.

Figure 11(1) shows the TPD profiles of H_2 adsorbed at 433 K followed by cooling down to room temperature on the pre-reduced/sulphided catalysts. Each of these profiles has mainly two peaks, i.e., peak-I centred at ~403 K and peak-II centred at 633–673 K. Conceivably, at the reaction temperatures for HAS (573–623 K for the present work), the surface concentration

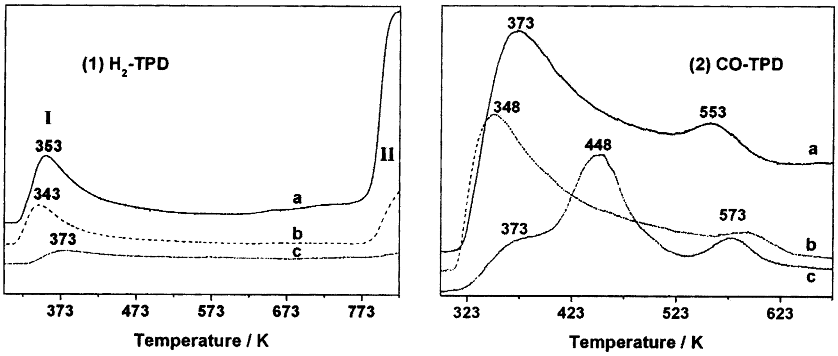

Figure 10. TPD profiles of adsorption of H_2 (1) or CO (2) on: (a) 6.4%Co/MWCNTs; (b) MWCNTs; (c) AC.

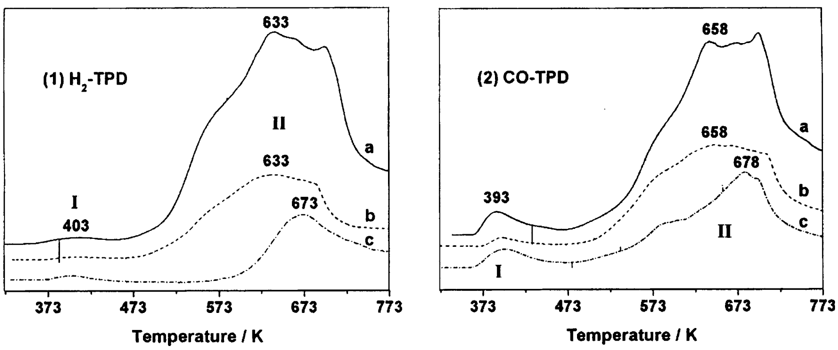

Figure 11. TPD profiles of adsorption of H_2 (1) or CO (2) on the pre-reduced/sulphided catalysts: (a) 11.6%($Co_1Mo_1K_{0.6}$)/(6.4%Co/MWCNTs); (b) 11.6%($Co_1Mo_1K_{0.6}$)/MWCNTs; (c) 50.3%($Co_1Mo_1K_{0.8}$)/AC.

of weakly adsorbed H-species associated with peak-I was expected to be very low, and most of H-adspecies at the surface of the functioning catalyst was associated with peak-II. Most likely it was those strongly adsorbed H-species that were related to the reaction activity of HAS. The relative area-intensity ratio of the peak-IIs of these H_2-TPD profiles for these catalysts was estimated to be: $S_{11.6\%(\mathrm{Co1Mo1K0.6})/(6.4\%\mathrm{Co/MWCNTs})}/S_{11.6\%(\mathrm{Co1Mo1K0.6})/\mathrm{MWCNTs}}/S_{50.3\%(\mathrm{Co1Mo1K0.8})/\mathrm{AC}} = 100/46/35$.

The analogous promoting effect was also observed in the adsorption of CO on these catalysts (see figure 11(2)). Under the same experimental conditions, the observed relative area-intensity ratio of the peak-IIs associated with desorption of strongly chemisorbed CO-species on these catalysts was estimated to be $S_{11.6\%(\mathrm{Co1Mo1K0.6})/(6.4\%\mathrm{Co/MWCNTs})}/S_{11.6\%(\mathrm{Co1Mo1K0.6})/\mathrm{MWCNTs}}/S_{50.3\%(\mathrm{Co1Mo1K0.8})/\mathrm{AC}} = 100/\ 68/66$.

Thus, the results of the TPD comparative investigations clearly indicated that the modification with the proper amount of metallic cobalt to the MWCNT-support led to a significant increase in adsorption capacity of the corresponding catalyst for H_2 and/or CO. The sequence of catalysts supported by the three supports in their capacity of adsorbing H_2 and/or CO was: 11.6% $Co_1Mo_1K_{0.6}$/(6.4%Co/MWCNTs) > 11.6%$Co_1Mo_1K_{0.6}$/MWCNTs > 50.3%$Co_1Mo_1K_{0.8}$/AC. This was in line with the sequence of the increasing specific reaction-activity of HAS over these catalysts.

It is quite evident that the high CO conversion, especially the high specific reaction-activity (see Table 3) and high selectivity to formation of C_{2+}-alcohols, in the HAS reaction over the sulphided $Co_1Mo_1K_{0.6}$ catalyst supported by Co-decorated MWCNTs is closely related to the peculiar properties of the Co-modified MWCNTs as support. Its excellent performance in adsorbing and activating the reactant molecules, H_2 and CO, and in promoting hydrogen-adspecies spillover is particularly important from a chemical catalysis point of view. Based upon the above TPD results, it could be inferred that, under the reaction condition of the HAS, there existed a considerably larger amount of reversibly adsorbed H-species and of CO-adspecies at the functioning surface of the sulphided Co–Mo–K catalyst supported by the Co-modified MWCNTs, which would help to generate the surface micro-environments with high stationary-state concentrations of H-adspecies and CO-adspecies on the catalyst. Through MWCNT-promoted hydrogen spillover, the H-adspecies could readily be transferred to $Co_iMo_jK_k$ active sites. These all would be in favour of increasing the reaction rate of CO hydrogenation-conversion at the surface of functioning catalyst. Moreover, the H-adspecies with higher stationary-state concentration at the surface of functioning catalyst would be in favor of inhibiting water-gas shift side-reaction, contributing considerably to an increase in the product yields. These are very similar to the cases of methanol synthesis over the MWCNT-promoted Cu–ZnO–Al_2O_3 catalyst [8, 9] and of higher alcohol synthesis over the MWCNT-promoted Co_iCu_j catalyst [10].

4. Concluding remarks

The present work shows that the Co-decorated MWCNTs could serve not only as a carrier, but also as an excellent promoter, of the sulphided $Co_iMo_jK_k$-based catalyst for HAS from syngas. Using the Co-decorated MWCNTs in place of simple MWCNTs or AC as the catalyst support resulted, on one hand, in a slight increase in the molar percentage of catalytically active Mo-species (Mo^{4+}) in the total Mo-amount supported and, on the other hand, in pronounced enhancement of the dissociatively adsorbed hydrogen H(a) and chemisorbed CO(a) at the surface of the functioning catalyst. All these play important roles in promoting the enhancement of activity of CO hydrogenation-conversion and the improvement of the selectivity of higher alcohol synthesis. For better understanding of nature of the promoting action by Co-modified MWCNTs, further studies, especially *in-situ* characterization of reaction intermediates under the HAS reaction condition, are highly needed.

Acknowledgments

The authors are grateful for the financial supports from National Natural Science Foundation (Projects No. 20473063 & 20590364) and National Basic Research ("973") Project (Project No. 2005CB221403) of China.

References

[1] K.P. de Jong and J.W. Geus, Catal. Rev.-Sci. Eng. 42 (2000) 481.
[2] P. Serp, M. Corrias and P. Kalck, Appl. Catal. A Gen 253 (2003) 337.
[3] H.B. Zhang, G.D. Lin, Y.Z. Yuan. *Current Topics in Catalysis*, Published by Research Trends, Vol.4 (2005) 1.
[4] J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P.M. Ajiayan, J. Am. Chem. Soc. 116 (1994) 7935.
[5] Y. Zhang, H.B. Zhang, G.D. Lin, P. Chen, Y.Z. Yuan and K.R. Tsai, Appl. Catal. A Gen 187 (1999) 213.
[6] Y. Cai, J.D. Lin, H.B. Chen, H.B. Zhang, G.D. Lin and D.W. Liao, Chinese Chem. Lett. 11 (2000) 373.
[7] E. van Steen and F.F. Prinsloo, Catal. Today 71 (2002) 327.
[8] H.B. Zhang, X. Dong, G.D. Lin, Y.Z. Yuan, P. Zhang, K.R. Tsai, in:*Utilization of Greenhouse Gases. ACS Symp. Ser. No.852*, C.J. Liu, R.G. Mallinson, M. Aresta, (eds.), (Washington DC: American Chemical Society, 2003), 195 pp.
[9] X. Dong, H.B. Zhang, G.D. Lin, Y.Z. Yuan and K.R. Tsai, Catal. Lett. 85(3–4) (2003) 237.
[10] H.B. Zhang, X. Dong, G.D. Lin, X.L. Liang, H.Y. Li. Chem. Commun. (2005) 5094.
[11] Z.J. Liu, Z.D. Xu, Z.Y. Yuan, D.Y. Lu, W.X. Chen and W.Z. Zhou, Catal. Lett. 72 (2001) 203.

[12] C.B. Li, W.X. Pan, W.K. Wong, J.L. Li, X.Q. Qiu and X.P. Chen, J. Mol. Catal. A Chem 193 (2003) 71.

[13] W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun and Q. Xin, Carbon 40 (2002) 791.

[14] E. Dujardin, T.W. Ebbesen, H. Hiura and K. Tanigaki, Science 265 (1994) 1850.

[15] T.W.J. Ebbesen, Phys. Chem. Solids 57 (1996) 951.

[16] L.M. Ang, T.S.A. Hor, G.Q. Xu, C.H. Tung, S.P. Zhao and J.L.S Wang, Carbon 38 (2000) 363.

[17] B. Xue, P. Chen, Q. Hong, J.Y. Lin and K.L. Tan, J. Mater. Chem. 11 (2001) 2378.

[18] Q.J. Quarderer, G.A. Cochran. Eur. Pat. Appl. 8, 410,932.5 (March 16, 1984); assigned to Dow Chemical Co.

[19] R.R. Stevens. Eur Pat. Appl. 84116467.6 (Dec. 28, 1984); assigned to Dow Chemical Co.

[20] N.E. Kinkade. Eur. Pat. Appl. 84116468.4 (Dec. 28, 1984); assigned to Union Carbide Coorporation.

[21] C.B. Murchison, M.M. Conway, R.R. Stevens, Q.J. Quarderer. *Proc. 9th Intern. Congr. Catal.* (Calgary, Canada) Vol.2 (1988) 626.

[22] J. G. Santiesteban, C. E. Bogdan, R. G. Herman, K. Klier. *Proc. 9th Intern. Congr. Catal.* (Calgary, Canada) Vol.2 (1988) 561.

[23] R.G. Herman, Stud. Surf. Sci. Catal. 64 (1991) 265.

[24] P. Forzatti, E. Tronconi and I. Pasquon, Catal. Rev Sci. Eng. 33 (1991) 109.

[25] A.B. Stiles, F. Chen, J.B. Harrison, X. Hu, D.A. Storm and H.X. Yang, Ind. Eng. Chem. Res. 30 (1991) 811.

[26] K.A.N. Verkerk, B. Jaeger, C.H. Finkeldei, W. Keim. Appl. Catal. A Gen 186 (1999) 407, and references therein.

[27] P. Chen, H.B. Zhang, G.D. Lin, Q. Hong and K.R. Tsai, Carbon 35(10–11) (1997) 1495.

[28] H.B. Zhang, G.D. Lin, Z.H. Zhou, X. Dong and T. Chen, Carbon 40(13) (2002) 2429.

[29] G.D. Zhou, *The basis of structure chemistry* (Beijing Univ. Press, Beijing, 1989).

[30] H.B. Zhang, X.M. Ma, B.S. Shen, H.Y. Li and G.D. Lin, Proc. Intern. Hi-Tech Symposium on Coal Chem. Ind. & Coal Convers., Zhongguo Meitan 30(Supp.) (2004) 223.

[31] Data base: Original ICDD PDF2 for X'Pert PRO X-ray Diffractometer (Panalytical, Netherlands).

[32] Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi and T. Kubota, Appl. Catal. A 226(1–2) (2002) 115.

[33] J. Abart, E. Delgado, G. Ertl, H. Jeziorowshi, H. Knözinger, N. Thiele, X.Z. Wang and E. Taglauer, Appl. Catal. 2 (1982) 155.

[34] Y. Ishikawa, L. G. Austin, D. E. Brown, P. L. Jr.Walker. in: *Chemistry and Physics of Carbon*, Vol.12, P. L. Jr.Walker, P.A. Thrower, (eds.), (New York: Marcel Dekker, 1975) 39 pp.

[35] Z.H. Zhou, X.M. Wu, Y. Wang, G.D. Lin and H.B. Zhang, Acta. Phys-Chim. Sin. 18(8) (2002) 692.