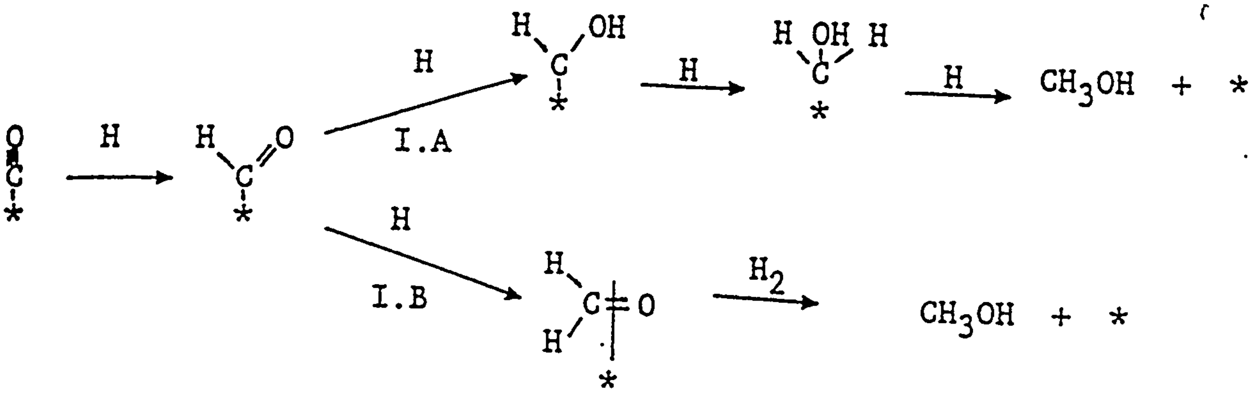
Activation and Incorporation of Carbon Monoxide

Of great importance in solving the mechanism of higher alcohol synthesis over alkali/MoS_2 are the questions of how carbon monoxide is activated and how the carbon monoxide is involved in chain propagation. In finding the actual sites of activation and propagation, the mechanism can be solved. There are two possible sites for activation and propagation. First is the alkali metal center, and the other is the molybdenum cations in the edge planes.

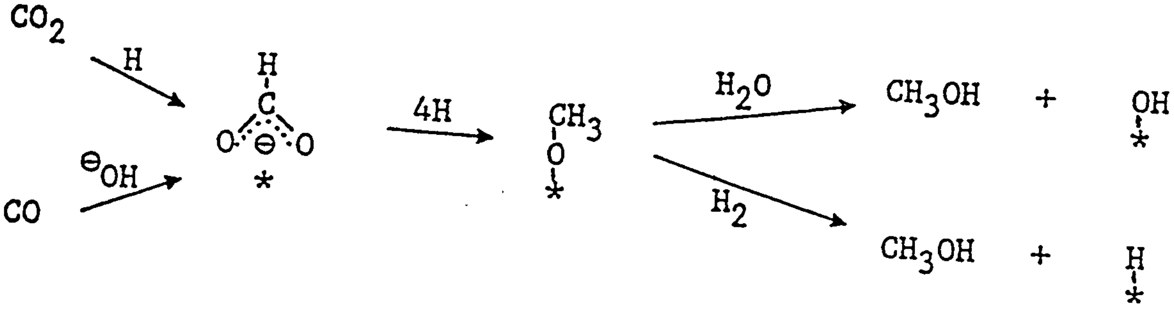
Mechanisms for Alcohol Synthesis From Synthesis Gas. The first step in alcohol synthesis is the activation of carbon monoxide. The two mechanisms usually considered involve either formyl or formate species. Reaction Scheme I shown on the next page is based on the formyl species stabilized on an active site (designated as *). The formyl species then can be further hydrogenated to give hydroxycarbene (I.A) or formaldehyde (I.B), which then can be farther hydrogenated to give methanol. Formyl species were identified by chemical trapping on nickel, rhodium, and palladium [29]. Formyl species have also been detected on Cu/ZnO using IR [30,31] and by trapping with amine [32]. In an isotope experiment over Rh/TiO_2 [33], a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ and hydrogen was passed over the catalyst. $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ were produced, but not $^{13}CH_3{}^{18}OH$ or $^{12}CH_3{}^{16}OH$. This was taken as evidence that the mechanism goes *via* formyl intermediate and excludes the formate pathway. The formate pathway would have caused isotope scrambling to give $^{13}CH_3{}^{18}OH$ and $^{12}CH_3{}^{16}OH$.

In Scheme II, either CO or CO_2 reacts with activated H to form a surface formate. This formate is then hydrogenated to form methoxide and then methanol. Formate and methoxide species have been detected by IR on ZnO [34], iron, nickel, and cobalt [35], magnesia [36], and alumina [37] following adsorption of methanol onto these materials.

SCHEME I



SCHEME II



Using the argument of microscopic reversibility, these intermediates must participate in methanol synthesis. High pressure *in-situ* IR spectroscopy has been employed using CO_2 and H_2 over $Cu/ZnO/Al_2O_3$ [38,39] and CO and H_2 over Cs/Cu/ZnO and Cs/ZnO [40]. In the last example, CsOOCH was detected through IR identification. Isotope experiments [41] were also carried out in which D_2O was injected into H_2/CO mixture to give $CH_2DO(H,D)$. It was concluded from this experiment that at least 65% of the methanol produced is formed *via* the formate mechanism.

It appears that on the noble metal catalysts, the main route to methanal is *via* the formyl pathway. However, on the Cu/ZnO-based catalysts, the main route to methanol can proceed *via* both formyl and formate intermediates.

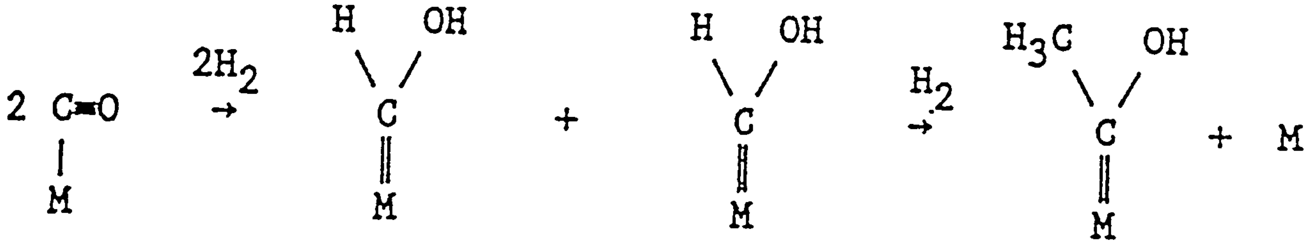
There are three main mechanisms for the production of linear alcohols. First is the condensation of alcohols proposed by Frolich and Cryder [42] and Graves [43]. It was proposed that higher alcohols are formed *via* condensation of lower alcohols according to the following reactions:

$$2\,CH_3OH \rightarrow CH_3CH_2OH + H_2O \qquad (1)$$

$$CH_3OH + CH_3CH_2OH \rightarrow CH_3CH_2CH_2OH + H_2O \qquad (2)$$

The second mechanism is enol condensation proposed by Anderson et al. [44,45] and Emmett et al. [46,47]. As seen in Scheme III, the methanol precursor is the chain initiator. The synthesis of C_2^+ alcohols occurs through hydroxycarbene intermediates followed by hydrogenation. Termination occurs by hydrogenolysis of the metal-carbon bond to form the corresponding alcohol. To account for the fact that hydrocarbons are also formed, the authors mentioned that adsorbed alcohols may be dehydrated to give hydrocarbons. The hydrocarbons would have the same chain growth probability.

Scheme III



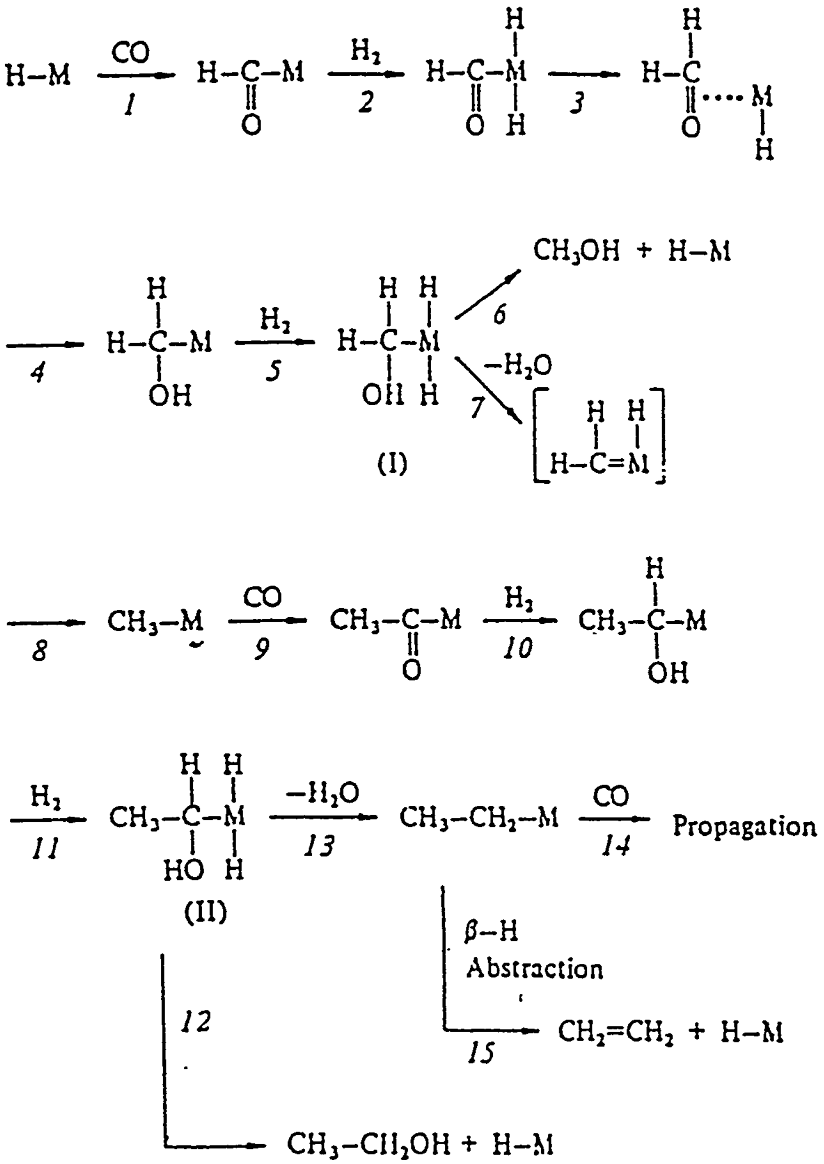
Lastly is the CO insertion mechanism, described by Fischer and Tropsch [48]. They suggested that the formation of higher alcohols occurs from methanol and carbon monoxide through the following reactions:

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (3)$$
$$CH_3COOH + H_2 \rightarrow CH_3CHO + H_2O \qquad (4)$$
$$CH_3CHO + H_2 \rightarrow C_2H_5OH \qquad (5)$$

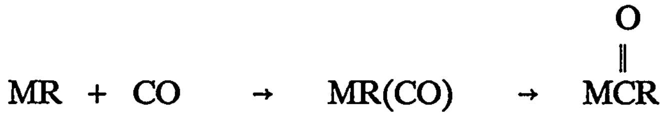
These reactions involve the insertion of CO into C-O bonds to form a carbon-carbon bond, followed by hydrogenation of the intermediate. The direct participation of alkali in the mechanism was proposed by Natta et al. [49]. It was proposed that an alkali alkoxide is formed using KOH/ZnO catalyst, which is then reacted with CO followed by rearrangement to give alkali carboxylate. This is followed by hydrogenation to give the corresponding alcohol. Kiennemann and Hindermann see the insertion of CO into a carbon-oxygen bond as unlikely, since there is no model known for this homogeneous catalysis [50]. It appears that the first to propose CO insertion into metal-carbon bonds was Wender et al. [51]. Henrici-Olive and Olive [52] and Pichler and Schulz [53] proposed mechanisms involving CO insertion into metal-hydrogen bonds for initiation, as well as CO insertion into metal-carbon bonds for chain growth. This is shown in Scheme IV.

Computational Aspects of CO Insertion. There are two possible sites for activation of CO and for chain propagation on alkali-doped molybdenum disulfide which have been alluded in the above discussion of mechanisms. The two sites are the molybdenum atoms on the edge planes and the alkali dopant. The first thing to be discussed will be computational studies of CO insertions on second row transition metals. Next will be experimental evidence for CO insertions. And last will be possible activation mechanisms of carbon monoxide.

SCHEME IV


H–M
CO
1
H–C–M
O
H2
2
H
H–C–M
O H
3
H
H–C
O····M
H
4
H
H–C–M
OH
H2
5
H H
H–C–M
OH H
(I)
6
CH3OH + H–M
–H2O
7
H H
H–C=M
8
CH3–M
CO
9
CH3–C–M
O
H2
10
H
CH3–C–M
OH
H2
11
H H
CH3–C–M
HO H
(II)
–H2O
13
CH3–CH2–M
CO
14
Propagation
β–H
Abstraction
15
CH2=CH2 + H–M
12
CH3–CH2OH + H–M

The reaction shown in Equation 6, where R = CH_3 or H, has been the focus of many theoretical studies using semiempirical and *ab initio* methods. Koga and Morokuma [54,55]



$$\mathrm{MR} + \mathrm{CO} \rightarrow \mathrm{MR(CO)} \rightarrow \mathrm{M}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R} \qquad (6)$$

have recently reviewed the computational studies done on the carbonyl insertion reaction. The subject of many of these studies has been why is the insertion of CO into metal-carbon bonds more preferred than CO insertion into metal-hydrogen bonds. The conclusion reached by several authors [54-56], is that the carbonyl insertion into metal-carbon bonds is thermodynamically favorable over carbonyl insertion into metal-hydrogen bonds. It is believed that the metal-carbon bond is weaker than the metal-hydrogen bond, however, there are also other factors that influence the energetics of the process. One factor is that there is a larger gain in energy for the formation of the C-H bond than for the formation of a C-C bond.

Another important aspect that must be considered in chemical reactivity and stability is that of the interaction of the lone pair of electrons on oxygen with the metal. Early metals, which are oxophilic, tend to form η^2-acyls and -formyls [57]. η^2-Acyls have been seen experimentally on early transition metals such as zirconium and titanium complexes by Fachinetti et al. [58]. This has been studied theoretically by several researchers with varying levels of approximation [59-61]. For $RMn(CO)_5$, Berke and Hoffmann, using extended Hückel computational analysis, found the η^1-complex to be more stable [59]. However, Ziegler et al., using a local density approach, found the η^2-complex to be more stable [60]. This result by Ziegler et al. was confirmed by Axe and Marynick using calculations at the Hartree-Fock level [61]. It appears that the more stable product is determined by the level of theory in the calculations.

In a study concerning the second row transition metals, Blomberg et al. [62] first investigated naked transition metal carbonyl complexes. Then, the effects of adding hydride or methyl ligands to the metal complexes were determined, after which calculations for the actual insertion reaction were carried out, and the barrier heights compared. The carbonyl binding energies are plotted in Figure 9. As can be seen, the largest (negative) binding energies are found at the right, with molybdenum having the smallest binding energy. The trend was explained to be the cause of two factors. First is the occupation of the metal d-shell, and secondly is the occupation of the 4s level. The 4s occupation is lower for elements on the right, leading to lesser repulsion of CO lone pair electrons. Also, for the elements to the right, the d- orbitals are doubly occupied leading to better back-donation. The elements to the left are only singly occupied. The elements to the left of molybdenum have the 4d-orbital unoccupied, and elements to the right can have the 5s state hybridize

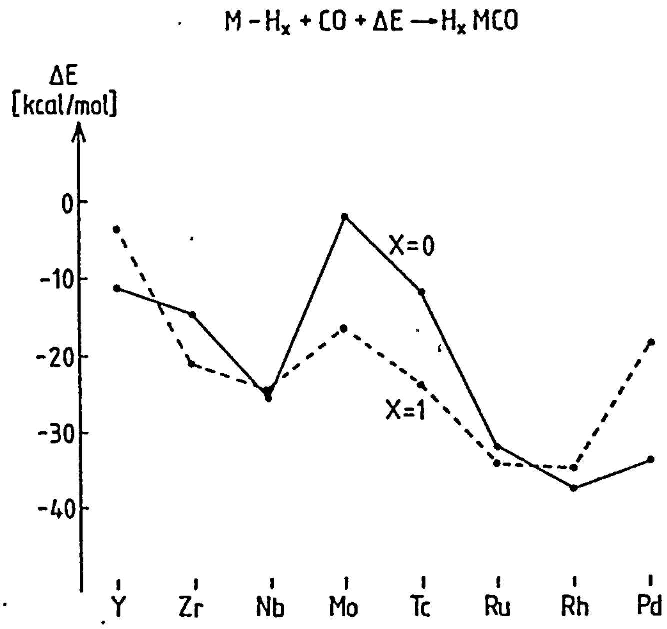


FIGURE 9. Calculated metal-carbonyl binding energies for naked metal atoms and for metal hydrides, relative to the free initial species [62].

away the repulsive electrons. Molybdenum is the only element in the second row to have both repulsive 5s- and 4d-orbitals occupied. This is why molybdenum has the lowest binding energy with CO in the second row. The addition of a hydride or methyl ligand substantially increases the carbonyl binding energies. This is due to the removal of an electron by the added ligand from the repulsive sd region.

In Figure 10, the barrier heights for carbonyl insertion into metal-carbon and metal-hydrogen bonds is shown [62]. The barrier heights for the insertion into the metal-carbon bond are always much higher than for the insertion into metal-hydrogen bonds. This is explained to be due to the metal-alkyl bond being more directional than the metal-hydrogen bond. From the calculations, it can be seen that the observation of CO inserting into M-C bonds rather than M-H bonds cannot be explained as a kinetic effect. Therefore, it must be concluded that it is a thermodynamic effect, in agreement with other studies [55-57].

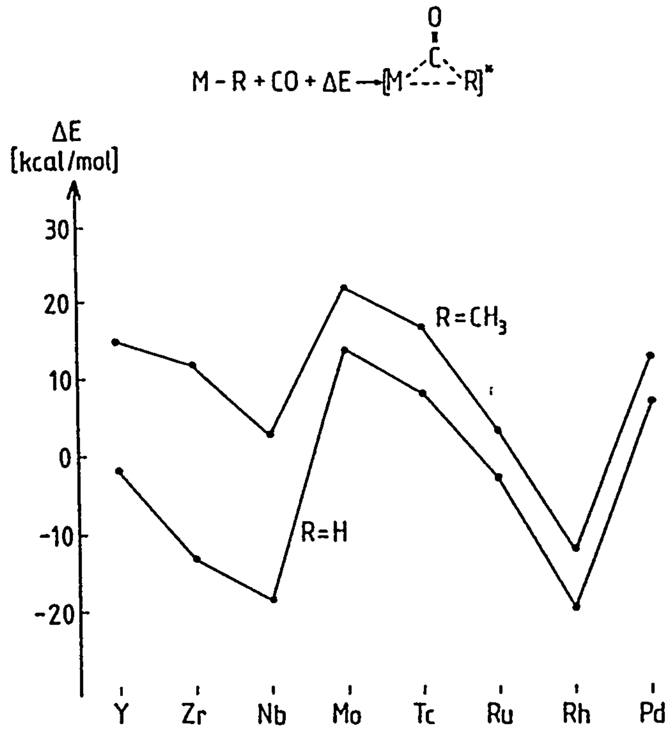


FIGURE 10. Transition state energies for carbonyl insertion into metal-hydrogen and metal-alkyl bonds [62].

As mentioned earlier, experimentally CO insertion into metal-carbon bonds is easier than the insertion into metal-hydrogen bonds. As seen in Figure 11, concerning the binding energies of the insertion product, the only metals for which the stabilities are considerably larger for acetyl than for the formyl complexes are ruthenium, rhodium, and palladium. For the rest of the metals, the stabilities are similar. The exception is zirconium, where the formyl is the more stable intermediate [62].

It can be concluded from these theoretical studies that insertion into metal-hydrogen bonds is unlikely when compared to the insertion of CO into metal-carbon bonds. This can be taken as evidence against the formyl mechanism, which involves the insertion of CO into a metal-hydrogen bond.

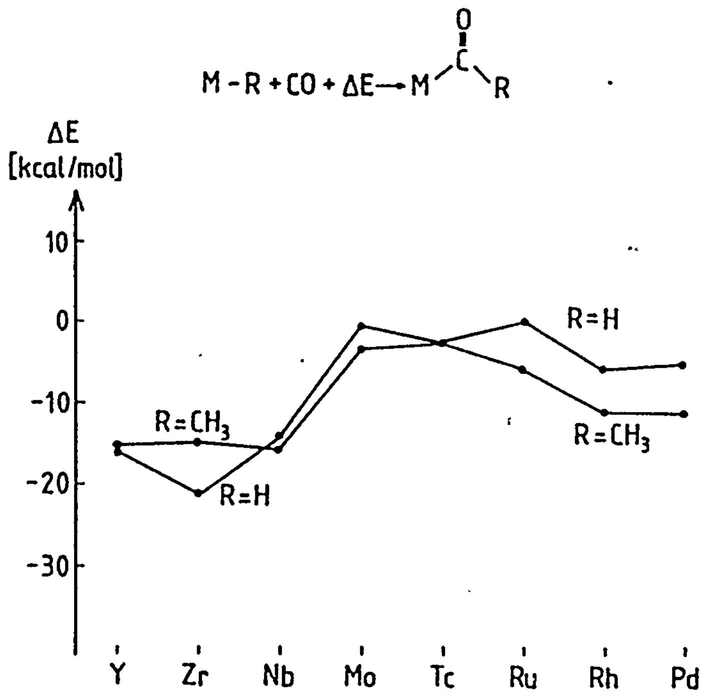


FIGURE 11. Reaction energies for carbonyl insertion into metal-hydrogen and metal-methyl bonds [62].

Experimental Evidence of CO Insertion. There are experimental examples of carbonyl insertion reactions occurring on molybdenum. For instance, CO will insert into a molybdenum methyl bond to give the acyl complex as shown in Equation 7 [63]. Equation 8 also shows another example of CO insertion into metal-carbon bonds. Incidentally, the rate of insertion is dependent of the substituent X on the benzyl group. Insertion is accelerated by electron-releasing and retarded by electron-withdrawing groups at the para position of the benzyl group [64].

$$\text{Me-MoCp(CO)}_3 + \text{PR}_3 \rightarrow \text{MeCO-MoCp(CO)}_2\text{PR}_3 \qquad (7)$$

$$\text{CpMo(CO)}_3\text{CH}_2\text{C}_6\text{H}_4\text{X} + \text{PPh}_3 \rightarrow \text{CpMo(CO)}_2\text{(PPh}_3\text{)(COCH}_2\text{C}_6\text{H}_4\text{X)} \qquad (8)$$

One experiment that gives substantial evidence that the mechanism for chain growth over the alkali-doped molybdenum disulfide catalyst proceeds *via* CO insertion was performed by Santiesteban et al. [11,27,65]. ^{13}C-labelled methanol that was enriched by a factor of 21.69 over the natural ^{13}C abundance of 1.11 atom% was used as a gas phase dopant. After reaching steady state synthesis conditions over a $CsOOCH/MoS_2 = 20/80$ wt% catalyst at the following conditions, $H_2/CO = 0.96$, 8.2 MPa, GHSV = 7465 ℓ/kg cat/hr, and temperature of 245-295°C, the labelled methanol was injected into the gas stream at a rate of 238.96 g/kg catalyst/hr. The liquid products were collected and analyzed by NMR and the gaseous products were analyzed by GC/MS. The enrichment factors for each carbon at various temperatures is shown in Table 6. It can be seen that the preferential enrichment occurred at the terminal carbons of the C_2-C_4 alcohols and at the methyl group of methyl esters and not at the carbonyl carbon. This result strongly suggests that the C_1 species initiates chain growth of C_2^+ alcohols and that the methyl group of methyl esters originates from methanol rather than from carbon monoxide. The labelled methanol is incorporated as in Equations 9-10.

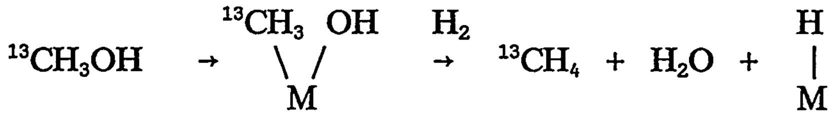
$$^{13}CH_3OH + {}^{12}CO/H_2 \rightarrow {}^{13}CH_3{}^{12}CH_2OH \quad (9)$$

$$^{13}CH_3{}^{12}CH_2OH + {}^{12}CO/H_2 \rightarrow {}^{13}CH_3{}^{12}CH_2{}^{12}CH_2OH \quad (10)$$

TABLE 6. Isotopic enriched of the carbon atoms in each product upon injection of $^{13}CH_3OH$ into the H_2/CO synthesis gas over a $CsOOCH/MoS_2$ = 20/80 wt% catalyst [11,27,65].

	^{13}C ENRICHMENT OF CARBON ATOMS			
Temperature (°C)	245	265	285	295
CH_3OH	17.7	14.2	11.9	7.4
CH_3	11.6	12.0	10.7	7.5
CH_2OH	1.3	1.4	1.5	1.1
CH_3	9.8	9.1	9.6	6.6
CH_2	-	-	2.4	1.8
CH_2OH	-	-	1.5	0.7
CH_3	-	-	9.0	5.9
CH_2	-	-	-	-
CH_2	-	-	-	-
CH_2OH	-	-	-	-
CH_3	21.8	26.2	18.9	25.7
O				
HC=O	-	-	-	-
CH_3	12.6	15.9	9.8	9.7
O				
C=O	-	-	-	-
CH_3	-	6.3	5.2	5.0

Further support for the CO insertion mechanism is provided by the observation that methane produced as a side-product was also labelled. The formation of methane is represented in Equation 11. This also supports the observation that in higher alcohol



$$^{13}\mathrm{CH_3OH} \rightarrow \underset{\mathrm{M}}{\overset{^{13}\mathrm{CH_3}\ \ \mathrm{OH}}{\diagdown\ \diagup}} \xrightarrow{H_2} {}^{13}\mathrm{CH_4} + \mathrm{H_2O} + \underset{\mathrm{M}}{\overset{\mathrm{H}}{|}} \qquad (11)$$

synthesis, the products follow the Shultz-Flory-Anderson distribution if both alcohols and hydrocarbons are included. If the chain growth mechanism went by either enol condensation or alcohol condensation, there would have been isotope scrambling. Therefore, the evidence strongly suggests chain growth occurs *via* CO insertion.

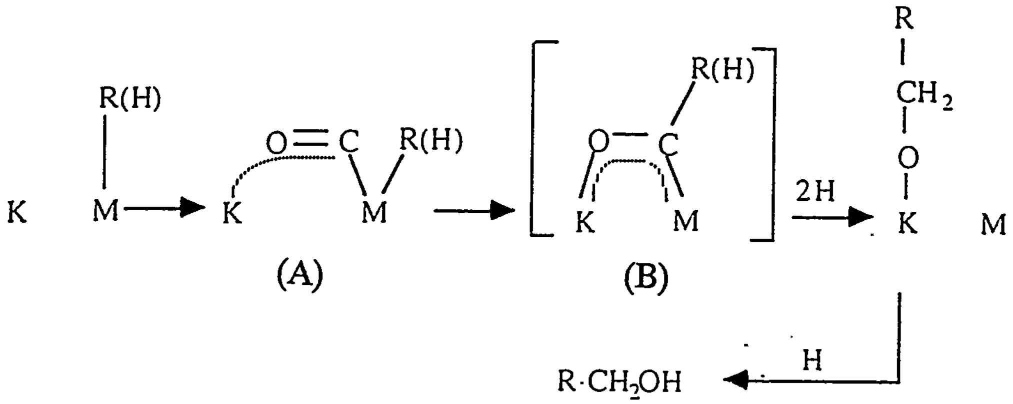
With the evidence suggesting that the mechanism for chain growth is via CO insertion, the site for this activity has to be determined. There are two possible sites for CO insertion. One is the coordinatively unsaturated molybdenum on the edge planes. The other is the alkali dopant. As stated earlier, there are examples of CO insertions occurring on molybdenum organometallic complexes. There is also evidence that alkali can undergo a similar reaction. Tonner et al. [66] have demonstrated that alcohols can be carbonylated in the presence of alkali metals. Those experiments were carried out in an autoclave using 100 ml of the alcohol at 50°C and pressurized to 4.0 MPa with 99.8% pure carbon monoxide. The catalyst consisted of alkali alkoxides dissolved in the corresponding alcohol to give concentrations of alkali between 0.3 and 1.0 M. The reactions were found to be first order with respect to carbon monoxide. The rate of the carbonylation reaction was found to increase in the order: methanol < ethanol < n-propanol < n-butanol < i-butanol < i-propanol < t-butanol < secondary butanol. The rate of reaction was found to be dependent upon the solubility of the carbon monoxide in the corresponding alcohol. The trend for solubility was found to be the opposite of the rate of carbonylation. The only products observed were the alcohol formates and a trace of alkali formate. The authors reported that the latter was problematic in that it reduced the amount of catalyst available. They suggested that the formation of the alkali formate came about from the reaction of the alkali hydroxide, caused by traces of water, and the alcohol as shown in Equation 12. However, the authors failed to give consideration to the formation of the alkali formates occurring through the reaction of CO and the alkali hydroxide, which is known to occur [67].

$$NaOH + HCOOR \rightarrow HCOONa + ROH \qquad (12)$$

If the CO insertion does not directly take place on the alkali on the catalyst, it may participate in the insertion of CO on the molybdenum as has been proposed by a number of researchers [25,68-69]. Klier et al. [68] suggested that the alkali assists in C-C bond formation on alkali/Cu/ZnO catalysts *via* β-addition with oxygen retention reversal in oxygenate synthesis. Woo et al. [25] and Sachtler et al. [69] have proposed that the role of the alkali cation is very similar in nature to that of a Lewis acid for insertion reactions on transition metals. Scheme V shows the reaction scheme proposed [25]. The CO and hydrogen ligands occupy coordination sites on the molybdenum disulfide with the alkali, K in this case, bound to the oxygen of carbon monoxide (A). The CO inserts into the metal carbon bond forming an intermediate acyl complex stabilized by the potassium (B). Butts et al. [70] have proposed that Lewis acids bound to the more basic oxygen of the acyl carbonyl group increases the rate of insertion and helps stabilized the unsaturated intermediate.

As far as the activation of carbon monoxide, the sites for activation could be the same as for the insertion reactions. As mentioned earlier, binding of carbon monoxide to

SCHEME V



a transition metal activates the carbonyl to nucleophilic attack at the carbon by hydroxide for example to give the formate. Also, carbon monoxide is known to form alkali formates when it reacts with alkali hydroxides [67]. There has been spectroscopic evidence for the alkali formates [40]. So the experimental evidence showing CO insertion to occur into molybdenum-carbon bonds and the absence of CO insertion into molybdenum-hydrogen bonds, as well as spectroscopic results showing alkali formates, and computational studies showing the preference of CO insertion into metal-carbon bonds strongly suggests that CO is activated by the alkali dopant. However, there is a possibility that is at least to some extent activated on the molybdenum edge atoms. The isotope experiments by Santiesteban et al. [11,27] strongly suggest that the chain growth goes *via* CO insertion. It has been proposed that the alkali participates in the insertion of CO.