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A New Aspect of the Pressure Effect in Syngas Conversion to Ethylene Glycol

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Synopsis. Pressure effect in syngas conversion to ethylene glycol (EG) is understood in terms of respective partial pressures of hydrogen (P_{H_2}) and carbon monoxide (P_{CO}). A new mechanism is proposed to explain an extraordinary effect of P_{H_2} on the selectivity to EG.

There has been observed a remarkable pressure effect on the rate and the selectivity of syngas conversion to ethylene glycol (EG) in the case of both cobalt,[1,2] and rhodium catalysis.[2,3] Although it has been presumed that both P_{H_2} and P_{CO} are responsible for this pressure effect, its dependency on each of them has never been fully established.[4] We have, therefore, undertaken to clarify the reason for this pressure effect by doing a series of experiments, varrying P_{H_2} at a fixed P_{CO}, and vice versa.

Results and Discussion

Cobalt-catalyzed reactions were performed in a mixed solvent consisting of phenol and *m*-cresol in a weight ratio of 5 to 1, since it is a good solvent for cobalt catalysis according to our previous exploration. While *N*-methyl-2-pyrrolidone (NMP) was used as a solvent for rhodium catalysis, since Rh–NMP is one of the well known system for the EG synthesis.[1] The results of experiments carried out with $Co_2(CO)_8$ 0.855 g (5 mg-atom as Co), phenol 25 g, *m*-cresol 5 g, under various P_{H_2} at 210 °C for 2 h, where P_{CO} was fixed at a constant, 150 kg cm^{-2}, are shown in Fig. 1. The dependency of the rate of EG formation on P_{H_2} is remarkable, the order of EG formation with respect to P_{H_2} being in the range of 2—3. On the other hand, almost linear relation is observed between the rate of methanol formation and P_{H_2}. As a result, the selectivity to EG increases and that to methanol decreases dramatically, as P_{H_2} is increased. The selectivity to methyl formate is almost independent of P_{H_2}.

The results of experiments carried out with $Rh(acac)_3$ 0.08 g (0.2 mg-atom as Rh), NMP 20 g, under various P_{H_2} at 260 °C for 2 h, where P_{CO} was fixed at a constant, 400 kg cm^{-2}, are shown in Fig. 2. As in the case of cobalt catalysis, the dependency of EG formation on P_{H_2} is fairly larger than that of methanol. The order of EG formation with respect to P_{H_2} is about 2, while the rate of methanol formation increases almost linearly with P_{H_2}. Consequently, the selectivity to EG increases and

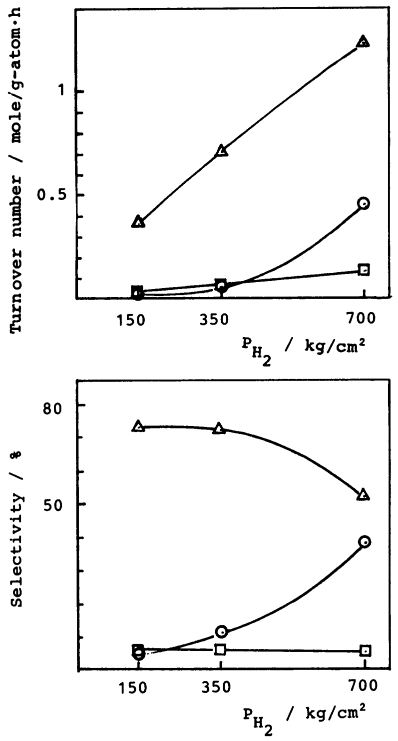


Fig. 1. Influence of H_2 partial pressure.
P_{CO}=150 kg cm^{-2}, 210 °C, Phenol 25 g+*m*-Cresol 5 g, Co 5 mg-atom, 2 h. Notations: ○ EG, △ MeOH, □ HCOOMe, Selectivity to EG (Sel_{EG})=2EG/A, Sel_{MeOH}=MeOH/A, Sel_{HCOOMe}=HCOOMe/A, A=2(EG+EtOH)+MeOH+HCOOMe.

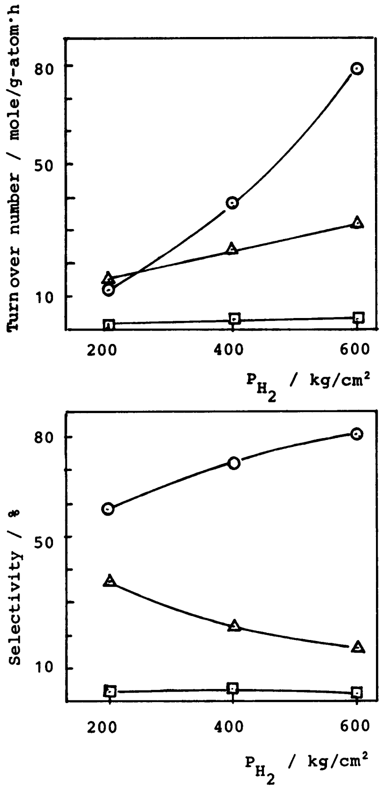


Fig. 2. Influence of H_2 partial pressure.
P_{CO}=400 kg cm^{-2}, 260 °C, NMP 20 g, Rh 0.2 mg-atom, 2 h. Notations: ○ EG, △ MeOH, □ GL (Glycerol), Sel_{EG}=2EG/B, Sel_{MeOH}=MeOH/B, Sel_{GL}=3GL/B, B=3GL+2(EG+EtOH)+MeOH+HCOOMe.

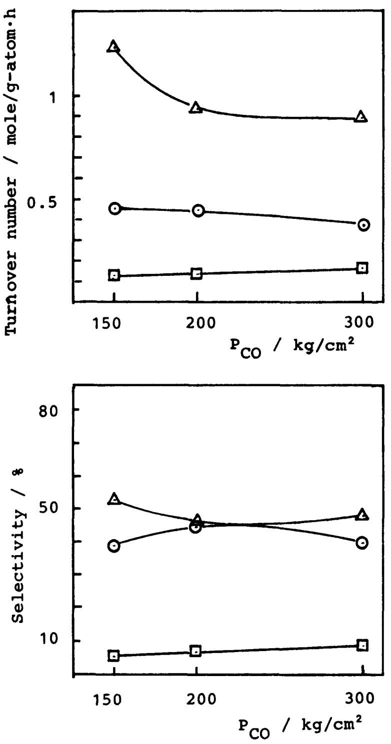


Fig. 3. Influence of CO partial pressure.
P_{H_2}=700 kg cm^{-2}, 210 °C, Phenol 25 g+*m*-Cresol 5 g, Co 5 mg-atom, 2 h. Notations: see Caption of Fig. 1.

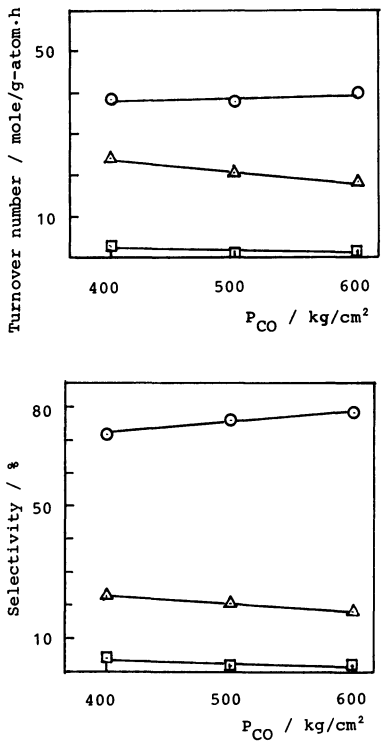


Fig. 4. Influence of CO partial pressure.
P_{H_2}=400 kg cm^{-2}, 260 °C, NMP 20 g, Rh 0.2 mg-atom, 2 h. Notations: see Caption of Fig. 2.

that to methanol decreases as P_{H_2} is increased. The selectivity to glycerol is almost independent of P_{H_2}.

The results of experiments carried out in the same manner as those shown in Fig. 1, except that P_{CO} was varied at a fixed P_{H_2}, 700 kg cm^{-2}, are shown in Fig. 3. The rate of EG formation is almost independent of P_{CO} in the range of 150—200 kg cm^{-2}, but it slightly declines as P_{CO} is increased above that range. On the other hand, the rate of methanol formation is independent of P_{CO} in the range of 200—300 kg cm^{-2}, whereas it sharply increases as P_{CO} is decreased below that range. As a result of these effects, the selectivity to EG showed a maximum and that to methanol a minimum, at the P_{CO} of about 200 kg cm^{-2}. The selectivity to methyl formate slightly increased with increasing P_{CO}. If value *A* (see caption of Fig. 1) is considered as representing the total CO hydrogenation activity, it is clear that the total rate of CO hydrogenation decreases as P_{CO} is increased.

The results of experiments carried out in the same manner as those shown in Fig. 2, except that P_{CO} was varied at a fixed P_{H_2}, 400 kg cm^{-2}, are shown in Fig. 4. Clearly, the rate of EG formation is almost independent of the P_{CO} in the range of 400—600 kg cm^{-2}, but the rate of methanol formation tends to decrease as P_{CO} is increased. As a consequence, the selectivity to EG slightly increases, and that to methanol declines as P_{CO} is increased. It is clear on calculating value *B* (see caption of Fig. 2), that the total rate of CO hydrogenation, in this case, is almost independent of P_{CO}.

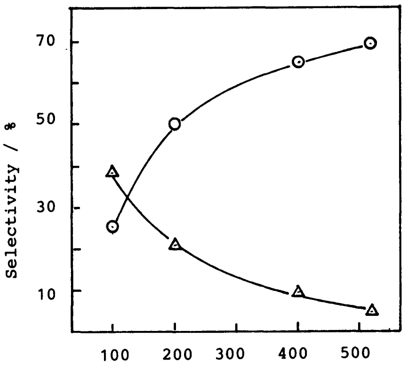
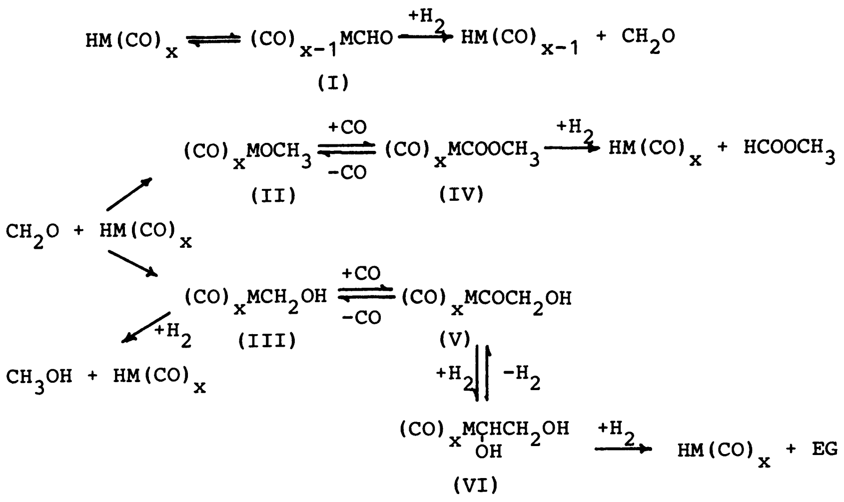


Fig. 5. Effect of H_2 partial pressure on the selectivity of the reaction of CH_2O with synthesis gas.
P_{CO}=100 kg cm^{-2}, 180 °C, CH_2O (37%aq) 40 mmol, Phenol 10 g+Toluene 10 g, Co 5 mg-atom, Ru 0.5 mg-atom, 2 h. Notations: ○ EG, △ MEOH.

In the course of our study of the cobalt catalyzed syngas reaction in the presence of formaldehyde, it was found that phenol–toluene mixture is a suitable solvent for EG formation,[5] and that the formation of unidentified products other than EG and methanol is dramatically suppressed by the presence of a small amount of ruthenium in addition to cobalt. Making use of these previous findings, the effect of P_{H_2} on the selectivity of syngas reaction with formaldehyde, where EG and methanol are the main products, was studied. The reactions were performed in an above mentioned solvent in the presence of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ in an atomic ratio of 10 to 1, where formaldehyde solution was fed, by means of a pump, to the reactor after the desired reaction temperature and pressure are reached in order to avoid the complexity arising from the reaction of formaldehyde occuring at a lower temper-



Scheme 1.

ature. The results are summarized in Fig. 5. A strikingly similar trend is observed as in the case of direct syngas conversion (cf. Figs. 1 and 2), i.e., the selectivity to EG increases and that to methanol decreases with increase in P_{H_2}.

Since a similar trend is observed in the P_{H_2} dependency of both cobalt- and rhodium-catalyzed reactions, the reactions in both cases are presumed to proceed by a generalized mechanism as shown in Scheme 1, where metal carbonyl hydride species is represented by $HM(CO)_x$ (M is Co or Rh). Formaldehyde intermediate, which is supposed to be produced by the hydrogenolysis of a formyl complex,[2] reacts with $HM(CO)_x$ to produce methoxy intermediate (II) and hydroxymethyl intermediate (III). EG and methanol is considered to be derived from a common intermediate (III), since there is always observed an opposite correlation between the selectivities of EG and methanol (cf. Figs. 1—4). On the other hand, methyl formate, the selectivity to which has any direct relation to neither EG nor methanol (cf. Figs. 1 and 3), is supposed to be derived from another intermediate (II). The hydroxyacetyl intermediate (V) is produced by the reversible addition of CO to intermediate (III), 1,2-dihydroxyethyl intermediate (VI) is produced by the reversible addition of H_2 to intermediate (V). Methanol is produced by the hydrogenolysis of intermediate (III), whereas EG is produced by the hydrogenolysis of intermediate (VI). Therefore, the order of EG formation with respect to P_{H_2} should be distinctively higher than that of methanol according to this scheme. Thus the reason for the effectiveness of hydrogen partial pressure on the EG selectivity is well understood by this mechanism.

Experimental

Apparatus. 100 ml Hastelloy C autoclave fitted with a stirrer; the autoclave is connected at the bottom through a valve to a gas-liquid separator, so that the reaction can be terminated at any desired time by opening the valve. The autoclave is brought to a desired temperature by heating under the pressure of CO or a mixed gas ($H_2/CO=1$), and pressure is readjusted to attain a desired P_{CO}. Then it is compressed with hydrogen to attain a desired P_{H_2}. Total pressure is kept constant (±20 $kg\,cm^{-2}$) by supplying a mixed gas ($H_2/CO=2$) during the reaction.

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