

STUDY ON THE MECHANISM FOR CLEAVAGE OF C-O BOND OF CO
AND THE RATE-DETERMINING STEP OF ETHANOL FORMATION IN
HYDROGENATION OF CARBON MONOXIDE ON RHODIUM CATALYSTS*

Haiyou WANG, Jinpo LIU, Jinlai XU, Jingkung FU,
Zhongyu LIN, Khirui TSAI

(The State Key Laboratory for Physical Chemistry of the Solid Surface,
Department of Chemistry, Xiamen University, Xiamen 361005, China)

Much attention has been dedicated in recent years to understanding the mechanism of ethanol synthesis from CO and H₂ over supported rhodium catalysts. There are divergent views on the mechanism of C-O bond cleavage. Some authors^[1,2] have suggested that C-O bond cleavage occurs via dissociation of adsorbed CO; while others^[3,4] have proposed that C-O bond cleavage occurs from a partially hydrogenated CO species (e.g. HCO , H_2CO , HCOH). In the present work, the main pathway for C-O bond cleavage and the rate-determining step involved in ethanol formation have been studied by using TPSR-IR dynamic method, Bond-Order-Conservation (BOC)-Morse potential approach and H₂/D₂ isotope effect.

The partially hydrogenated CO species, HCO (1592cm⁻¹), and CH_2 species (2933cm⁻¹) are simultaneously detected by IR in CO adsorption-TPSR (in H₂ flow) dynamic process over Rh-Mn(1:1)/SiO₂ catalyst, and a good correlation between the detected surface formyl and the ethanol activity is also observed, implying that formyl species is a key intermediate in the ethanol synthesis and that C-O bond cleavage occurs from a partially hydrogenated CO species. BOC-Morse potential approach predicts the activation energies for C-O bond cleavage on Rh (111) surface according to dissociation mechanisms (including direct and hydrogen assisted dissociation of adsorbed CO) and association mechanisms (including direct and hydrogen assisted dissociation of partially hydrogenated CO such as HCO , H_2CO , HCOH), showing that the activation energy for hydrogen assisted dissociation of H_2CO (or HCOH) is lowest. Based on the results of IR and BOC calculation, it may be concluded that C-O bond cleavage occurs via hydrogen assisted dissociation of partially hydrogenated CO species.

H₂/D₂ isotope effects in syngas conversion reaction have been investigated by performing CO + H₂ and CO + D₂ reaction alternatively. Noticeable deuterium inverse isotope effects both on methanol and on ethanol formation are simultaneously observed over V- and Mn-promoted rhodium catalysts, implying that the rate-determining steps involved in both methanol formation and ethanol formation are very probably, in each case a step of hydrogenation. Combined with the result of BOC calculation, it is suggested that H_2CO (or HCOH) + H → CH_2 + OH is probably the rate-determining step involved in ethanol formation reaction over rhodium catalysts.

References

- [1] W.M.H. Sachtler, Proc. 8th Int. Congr. Catal., 1984, 1:15
- [2] M. Ichikawa, CHEMTECH, 1982:647
- [3] Khirui Tsai et al., J. Phys. Chem. (Chinese), 1985, 1:177
- [4] V.L. Kuznetsov et al., Proc. 8th Int. Congr. Catal., 1984, 5:3

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