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SELECTIVITIES OF GROUP VIII METALS FOR THE HYDROGENATION OF FORMALDEHYDE AND THE EFFECT OF SUPPORT AND PROMOTER

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The reaction of HCHO over group VIII metals was studied. The main products obtained with powder catalysts were CO and CH_3OH, while CH_4 was formed at higher temperatures. The CH_3OH selectivity of the powder catalysts correlated well with the heat of formation of oxide. Although the SiO_2 support did not affect the CH_3OH selectivity of the metal, ZnO and Cs_2O improved it remarkably. Cu-Zn-Al catalysts are quite active for CH_3OH formation.

The question of the intermediate (dissociative or associative) of the CO hydrogenation reaction has been under debate. While the dissociative mechanism seems to be prevalent in the case of methanation over Fe, Co, Ni, or Ru catalysts,[1] the associative mechanism is important for methanol synthesis.[2,3] Since adsorbed formyl, CHO(a), is believed to be an active intermediate of the associative mechanism, it is interesting to study the reactivity and selectivity of metals for the HCHO reaction and to study the effect of the support and the promoter with respect to the CO hydrogenation mechanism.

A pulse of 0.4 μl of 35% HCHO aqueous solution containing 13.4% CH_3OH as a polymerization inhibitor was injected in a stream of H_2 in a micro pulse reactor system. Products were analyzed gaschromatographically by a column down-stream of the micro reactor. Since the reactivity of CH_3OH over metals was much less than that of HCHO (practically no reaction up to 200°C), the effect of CH_3OH in the HCHO solution could be ignored below ca. 300°C.

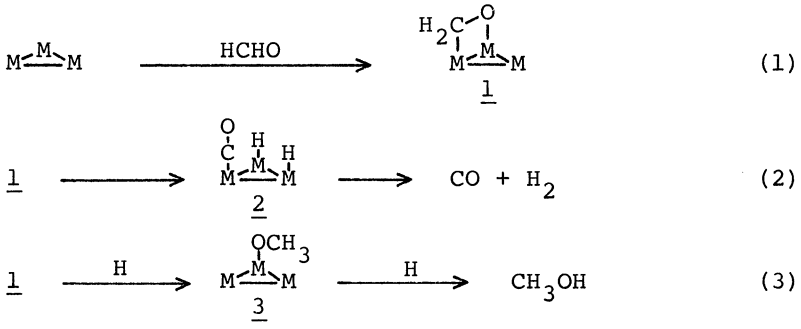
Nine group VIII metals (powders or sponges except for Fe, mostly 20 mg each) were tested without support following H_2 reduction at 400°C for 1h. The major products were found to be CO and CH_3OH over the temperature range 100 to 300°C. Methanol yields were maximum at around 250 to 300°C, while CO production increased with temperature. In the case of iron, Fe_2O_3 was reduced at 450°C and then used for the reaction.

Table 1. Activity and selectivity of metal powder for HCHO hydrogenation

Metal	Pd[c]	Ru	Co	Pt	Ni	Rh[d]	Os	Ir	Fe
surface area (m^2/g)	--	0.90	0.22	--	--	0.04	0.51	0.27	--
Activity (% conv.)[a]	100	96	83	65	39	27	18	10	10
% Selectivity for CH_3OH[b]	22	23	47	52	25	19	57	46	74

a) at 250°C over 20 mg of metal. b) at 15% conversion. c) 40 mg of wt.
d) 150 mg of wt. because of the small surface area.

Reduction temperatures above 300°C did not affect the catalyst selectivity. The results are summarized in Table 1. Activity sequencies did not correlate with those for formic acid decomposition on metals.[4] Considering that formaldehyde functions as a dihapto ligand in an osmium complex and does as a bridging ligand in a binuclear complex,[5] HCHO is considered to react on metal powder as follows;[6]



Since methanol selectivity is considered to be related to the stability of 3 against that of 2, the heat of formation of metal oxide per metal atom ($-\Delta H_o^\circ$)[7] was evaluated as an index of the M-O bond strength. The CH_3OH selectivity was plotted as a function of $-\Delta H_o^\circ$ as shown in Fig. 1, and a good correlation was found apart from Pt.

Methane production was observed above 250°C over Ru, above 350°C over Co, and above 400°C over Ni powder at which temperature HCHO conversion reached ca. 100%. The methane yield from HCHO pulse injection and the CH_4 yield from CO pulse injection were similar in magnitude over these metal powders, which suggests that CH_4 is formed from decomposed CO and that adsorbed formaldehyde (1) is not an intermediate of methanation from CO and H_2.

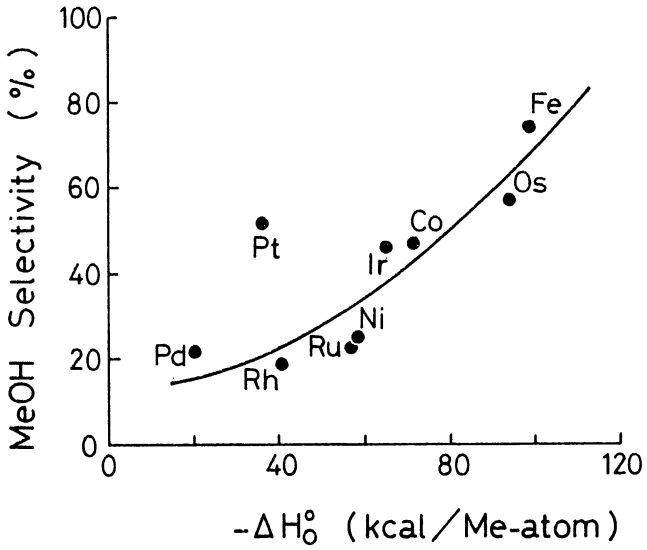
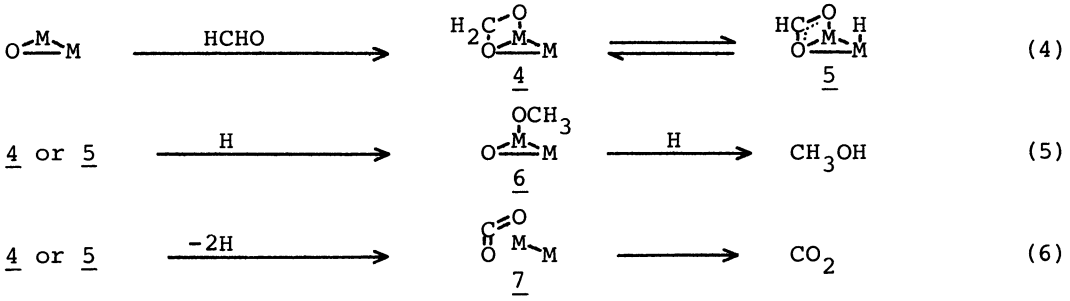


Fig.1. Methanol selectivity of group VIII metals in the hydrogenation of formaldehyde as a function of heat of formation of metal oxide per metal atom.

In order to check the effect of the support or promoter on the reaction, SiO_2 supported 5wt%Ru, 2wt%Rh, 2wt%Pt catalysts, ZnO supported 2wt%Ru, 2wt%Rh, 2wt%Pt catalysts, and Cs_2O added Ru catalyst (Ru powder and 5%Ru-SiO_2) were used following H_2

reduction at 300°C or in some cases at 400°C. Some of the results are shown in Fig. 2 as a function of temperature. The selectivity for methanol formation at 50% conversion is shown in Table 2. SiO_2 produced high metal dispersions and high activities but exhibited similar CH_3OH selectivities to the powders. ZnO or Cs_2O produced high CH_3OH selectivities as indicated in Table 2. Since metal powder has a lower CH_3OH selectivity and ZnO or Cs_2O has no CH_3OH formation activity from HCHO under temperatures of ca. 300°C, their combination is considered to produce a new function. When using ZnO supported or Cs_2O added metals, which produces higher CH_3OH selectivities, CO_2 production is observed namely 3% yield at 300°C, 5% at 350°C on Ru-ZnO, 2% at 250°C, 8% at 350°C on Pt-ZnO, and 1% at 300°C on Rh-ZnO. If CH_3OH and CO_2 originate from a common intermediate, formaldehyde must be adsorbed on oxygen which might become one of the oxygen atoms in the generated CO_2. As it has been reported that formate ions are formed from CH_3OH on ZnO[8] or from H_2/CO on $Ru-SiO_2$,[3] the following mechanism is proposed.



These mechanism (4 to 6), in which metal and oxide forms an active center, would be important for methanol synthesis from H_2/CO because the combination of metal and basic support has been reported to be important for alcohol synthesis from H_2/CO.[9]

Table 2 Methanol selectivities (%) of supported metals at 50% conversion

Catalyst	Ru	Rh	Pt
Powder	15	7	35
Me-SiO_2	--	7	44
Me-ZnO	41	45	81
Me-Cs_2O	23[a], 84[b]		

a) $Ru-SiO_2-Cs_2O$, b) data at 20% conversion

A highly active catalyst (Cu-Zn-Al) for methanol synthesis from CO/H_2, which has been studied with respect to surface properties,[10] was used for formaldehyde hydrogenation after reduction at 300°C for 1h. Twenty mg of the sample (60Cu-35Zn-5Al) was so active as to give 100% conversion at 150°C. Strong absorption of the reactant prevented chromatographic analysis under 150°C. The products at 150°C were CH_3OH and CO_2 with trace amounts of CO and methylformate; 20 to 40% of the HCHO was left on the catalyst. Methanol selectivities among the products were 77 (60Cu-35Zn-5Al) to 92%(95Zn-5Al). A similar mechanism to Eq. (4 to 6) should be applicable in this case although the role of each component (Cu-Zn-Al) is not clear.

The authers wish to acknowledge the help of Dr. K. Shimomura who provided the methanol catalysts.

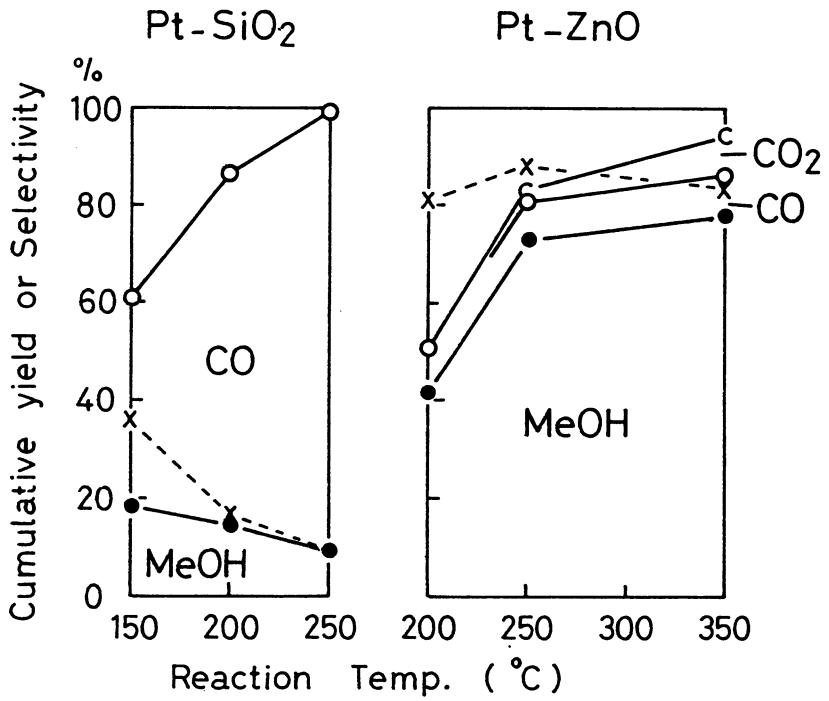


Fig. 2. Cumulative yields of methanol(●), carbon monoxide(o), and carbon dioxide(c), and selectivity of methanol(X) in the reaction of hydrogenation of formaldehyde over 2%Pt catalysts (40 mg).

References

1) P. Biloen, and W. M. H. Sachtler, "Adv. Catal.", vol. 30, p165, Academic Press, New York 1981,
A. T. Bell, "Catal. Review", vol. 23, p203, Marcel Dekker, New York, 1981.
2) M. L. Poutsma, L. F. Elek, P. A. Ibarbia, A. P. Risch, and J. A. Rabo, J. Catal., 52, 157 (1978),
F. Fajula, R. G. Anthony, and J. H. Lunsford, J. Catal., 73, 237 (1982),
A. Takeuchi and J. R. Katzer, J. Phys. Chem., 85, 937 (1981).
3) Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, J. Chem. Soc. Farad. Discuss., 72, 135 (1981).
4) W. M. H. Sachtler, J. Fahrenfolt, Proc. 2nd Intern. Congr. Catal., Editions Technip Paris 1961, vol. 1, p831.
5) K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, J. Amer. Chem. Soc., 101, 503 (1979),
P. T. Wolczanski and J. E. Bercaw, Acc. Chem. Res., 13, 121 (1980).
6) J. B. Benzinger, and J. R. Madix, J. Catal., 74, 55, 67 (1982).
7) K. Tanaka and K. Tamaru, J. Catal., 2, 366 (1963).
8) A. Ueno, T. Onishi, and K. Tamaru, Bull. Chem. Soc. Japan, 43, 2652 (1970).
9) M. Ichikawa and K. Shikakura, Proc. 7th Int. Congl. Catal., Kodansha-Elsevier Pub, Tokyo-Amsterdam, 1981, p925.
10) K. Shimonura, K. Ogawa, M. Oba, and Y. Kotera, J. Catal., 52, 191 (1978).

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