Volcano-shaped Relation between Heats of Oxide Formation of Metals and Coal-liquefaction Activities of Liquid-metal Catalysts

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Summary Plots of coal-liquefaction activities of molten Zn, Cd, Ga, In, Tl, Bi, Sn, and Pb against the heats of oxide formation of these metals exhibited a volcano-shaped relationship which suggests that the interactions between the atoms of the catalyst metal and the oxygen atoms which link the structural units of coal are one of the important factors which determine coal-liquefaction activity.

Coal liquefaction is an important technological problem and intensive experimental work has been undertaken using various heterogeneous catalysts.[1,2] One severe disadvantage encountered in coal liquefaction with a traditional heterogeneous catalyst is that of catalyst fouling[1,3] by the reactant coal and the fragments produced during the reaction. To circumvent this disadvantage, which often obscures the intrinsic mechanism of catalytic coal-liquefaction, the use of liquid metals for the reaction has been examined, since liquid-metal catalysts are, in general, affected little by the deposition of carbonaceous material if an appropriate experimental method is used.[4] The details of the experimental results will be reported elsewhere[5] and the most important aspect of coal-liquefaction activity of liquid-metal catalysts is reported herein.

The experiments were carried out using 'New Yubari Coal' as the reactant (elemental composition, C, 86·1; H, 6·1; O, 5·5; S, 0·3; and N, 2·0 wt %). The purity of each catalyst metal was better than 99·9%. The liquefaction was carried out for 4 h under pre-determined optimal conditions [T, 400 °C; stirring rate, 250 r.p.m.; weight of catalyst, 50 g; weight of coal, 10 g; initial pressure of hydrogen, 80 kg cm^{-2} (at room temperature)]. The gaseous product was analysed by gas chromatography and the liquid product was fractionated into an oil fraction, a hexane-soluble (H.S.) fraction, and a benzene-soluble (B.S.) fraction, by the procedure reported in the literature.[6]

Activities of the liquid-metal catalysts are summarized in the Table. It is evident that the liquid-metal catalysts are effective for coal liquefaction. Every catalyst gave liquefaction conversions higher than that of the non-catalytic reaction. It is also noteworthy that the catalysts were essentially inactive for the gasification of coal.

Table. Coal-liquefaction activities of liquid metals.

	Liquefaction				Gasification				
Catalysts	Oil	H.S.	B.S.	Total	CH_4	C_2H_6	C_3H_8	C_4H_{10}	Total
		(wt %)					(wt %)		
Zn[a]	15·5	10·1	30·0	55·6	4·9	2·2	2·1	1·4	10·6
	12·8	8·4	32·8	34·0	6·8	3·6	3·2	1·8	15·4
Bi	7·0	5·1	34·9	47·0	3·7	1·7	1·3	0·8	7·5
In	14·7	8·5	21·8	45·0	4·7	2·3	1·8	1·3	10·1
	15·9	5·5	21·9	43·3	4·8	2·4	2·1	1·3	10·6
Sn	5·6	1·5	34·8	41·9	3·5	1·6	1·4	0·9	7·4
	13·2	6·8	25·5	45·5	4·5	2·4	1·9	1·2	10·0
Cd	8·9	5·4	23·0	37·3	4·4	1·9	1·6	1·1	9·0
Tl	15·5	4·6	9·2	29·3	3·9	2·3	2·3	1·5	10·0
Pb	9·2	3·7	16·7	29·6	3·2	1·9	1·6	1·1	7·8
Ga	4·7	3·0	11·6	19·3	1·9	0·9	0·7	0·5	4·0
None	4·0	2·4	0·3	6·7	2·4	1·2	1·1	0·8	5·5

[a] Values at 420 °C (m.p. of zinc): extrapolation to 400 °C gives *ca.* 62 wt % liquefaction and *ca.* 8 wt % gasification.

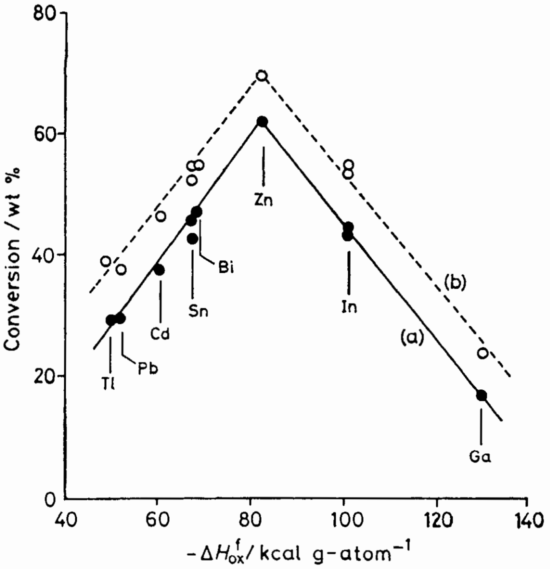

FIGURE. Volcano-shaped relation between coal-liquefaction activities of the liquid metals and the heats of oxide formation ($-\Delta H^{f}_{\mathrm{ox}}$) of the catalyst metals. (a) Liquification; (b) total conversion; the value for Zn is extrapolated.

The most interesting result obtained in the present work is shown in the Figure. Plots of liquefaction activities of the liquid metals against heats of oxide formation ($-\Delta H^{f}_{\mathrm{ox}}$) of the catalyst metals exhibited a volcano-shaped relation (because of the reducing atmosphere, $-\Delta H^{f}_{\mathrm{ox}}$ for the lowest oxidation state was adopted for multivalent metals). No good correlation was obtained when any other property characteristic of the metal or the liquid metal was used instead of $-\Delta H^{f}_{\mathrm{ox}}$.

It appears that the ordinate of the Figure is a measure of the intrinsic activity of the catalyst metal; the conversion value given on the ordinate is that for the catalyst:coal weight ratio of 5. The liquefaction conversion for the Sn catalyst was almost constant if catalyst:coal $\geqslant 2$ (weight ratio); liquefaction conversions of 44, 42—46, and 38 wt % were obtained with catalyst:coal weight ratios of 2, 5, and 10, respectively. This suggests that when the catalyst:coal weight ratio is 5, the amount of catalyst metal is sufficient to react with all the reactive sites which exist in the coal structure, and hence the catalytic activity observed reflects directly the turnover frequency of the reaction between the catalyst atom and the reactive site.

It is well known[7] that macro-molecules which constitute the coal structure have various kinds of links which contain oxygen. It is conceivable that the area around such a link is the reactive site of coal. Thus, if scission of this link determines the rate of coal liquefaction, a volcano-shaped relationship between liquefaction activity and the heat of formation of the oxide of the catalyst metal would be expected. For a metal of small $-\Delta H^{f}_{\mathrm{ox}}$, a weak interaction between the metal atom and the active site is expected. In this case a low catalytic activity would occur. On the other hand, a strong interaction between the catalyst atom and the active site is expected for catalyst metals of large $-\Delta H^{f}_{\mathrm{ox}}$. However, if the interaction is too strong the catalyst atom and the oxygen-bearing fragment produced by the scission of the reactive link would form a stable complex. This hinders the reaction and results in a small turnover frequency. For these reasons it is expected that metals of appropriate $-\Delta H^{f}_{\mathrm{ox}}$ will exhibit high catalytic activities for coal liquefaction.

The discussion above is by no means conclusive. Further studies are necessary, in order to make an unambiguous interpretation of the volcano-shaped relationship. Study of liquid-metal catalysis of the decomposition of a compound[8] which models the reactive part of the coal structure may enable this.

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