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An MO-theoretical Account of the Catalytic Property of Transition-metal Carbides and Nitrides in Dehydrogenation Reactions

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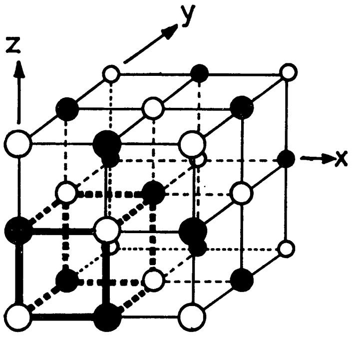
Refractory compounds of transition-metal carbides and nitrides have been pronounced to be catalysts possessing high catalytic activity in the dehydrogenation of ethylbenzene,[1] cyclohexane,[2] *etc.*, while those of transition-metal borides have proved to be quite inactive.[2] The catalytic properties of refractory compounds, however, have not yet been strictly established on a molecular level. The present study was undertaken in an attempt to correlate the electronic states of transition-metal carbides and nitrides and their catalytic properties in the dehydrogenation reactions, using the all-valence-shell-electron extended Hückel MO (EHMO) method[3] involving metal *d*-orbitals. The FCC NaCl-type carbides and nitrides (named MC and MN respectively) of TiC, VC, ZrC, NbC, HfC, TaC, TiN, VN, CrN, ZrN, NbN, and HfN have been studied; a simple model of their solid states for the EHMO calculations is presented in Fig. 1 and in Table 1.



○: metal
●: carbon or nitrogen

Fig. 1. Calculated model (enclosed by thick solid- and dotted-lines) of FCC NaCl-type transition metal carbides and nitrides.

Table 1. Bond distances[a] of M–C and M–N

MC	M–C (Å)	MN	M–N (Å)
TiC	2.1658	TiN	2.12
VC	2.091	VN	2.065
ZrC	2.349	ZrN	2.28
NbC	2.235	NbN	2.19
HfC	2.314	HfN	2.26
TaC	2.227	CrN	2.08

a) Taken from H. F. Mark, J. J. McKetta, Jr., and D. F. Othmer, "Encyclopedia of Chemical Technology," 2nd, Ed., Vol. 4, (1964), p. 13.

First, let us discuss the correlation between the atomic charges of M in MC or MN and the rate constants,[1] *k*, reflecting the catalytic activity in the dehydrogenation of ethylbenzene at 560 and 600°C. As Fig. 2 indicates, the MC series tested showed the formal charges of M in the range of *ca.* +0.3—3.5 and gave a maximum indicative of their catalytic activities near the tri-valent charge of M (transition metal).

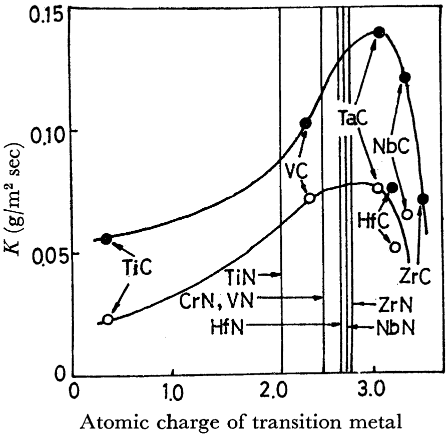


Fig. 2. Correlation between the catalytic activities of transition metal carbides and nitrides and the atomic charges of their metals.
○: 560°C; ●: 600°C

Next, a more precise discussion will be undertaken. The transition-metal carbides and nitrides are characterized by the lowest unoccupied (LU), triply-degenerate d_{xz}, d_{yz}, and d_{xy} metal–orbitals, and also by the LU+1, doubly-degenerate $d_{x^2-y^2}$ and d_{z^2} metal–orbitals. The net orbital populations of the *s* and *p* orbitals of metal and carbon (or nitrogen) atoms at the highest occupied (HO) or the LU level are negligibly small. This implies that the *s* and *p* orbitals cannot participate directly in the electron donor-acceptor process between the catalyst and such reactants as ethylbenzene. Table 2 lists the orbital populations of the d_{xz}, d_{yz}, and d_{xy} orbitals on the metal at the triply-degenerate levels (denoted as $1/2N_{xz}$, $1/2N_{yz}$, and $1/2N_{xy}$ respectively)

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[1] G. V. Samsonov, T. G. Bulankova, P. A. Khodak, E. M. Preshedromirskaya, V. S. Sinel'nikova, and V. M. Sleplosov, *Kinet. Katal.*, **10**, 1057 (1967).

[2] A. A. Balandin, Editor, "Scientific Selection of Catalysts," (translated from the Russian), Israel Program for Scientific Translations, Jerusalem (1968), p. 263.

[3] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1964): the ionization energies (eV unit) of the outer *s*, *p*, and *d* shells for Coulomb integrals of transition metals were taken from Moor's table (C. E. Moor, "Atomic Energy Levels," Natl. Bur. Std. Circ., No. 467 (1958), Vols. 1, 2, and 3) as follows: 10.33, 6.38, and 11.84 for Ti; 8.0, 6.0, and 10.0 for V; 8.0, 7.0, and 9.0 for Cr; 7.14, 4.78, and 7.14 for Zr; 7.58, 4.99, and 7.58 for Nb; 7.87, 5.87, and 7.87 for Hf; 8.14, 5.15, and 8.14 for Ta.

Table 2. Electronic states of transition metal carbides and nitrides

MC or MN	Bond population of M–C or M–N	Net orbital populations at degenerate levels	
		$1/2N_{xz}=1/2N_{yz}$ $=1/2N_{xy}$	$1/2N_{x^2-y^2}$ $=1/2N_{z^2}$
TiC	0.438	0.1421	0.0355
VC	0.438	0.2324	0.0252
ZrC	0.241	0.1449	0.0322
NbC	0.296	0.2397	0.0153
HfC	0.363	0.1351	0.0461
TaC	0.364	0.2389	0.0157
TiN	0.287	0.2432	0.0084
VN	0.217	0.2447	0.0075
ZrN	0.106	0.2453	0.0073
NbN	0.133	0.2455	0.0065
HfN	0.173	0.2444	0.0008
CrN	0.235	0.2109	0.0575

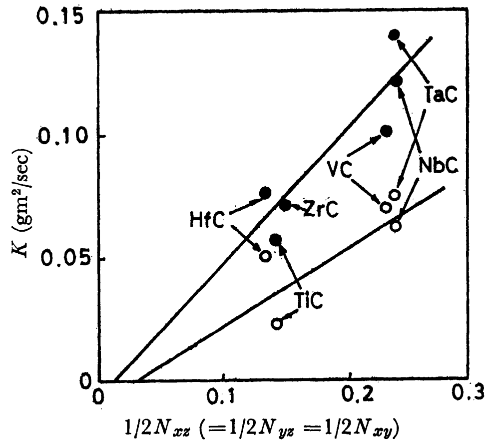

Fig. 3. Correlation between the catalytic activities of transition metal carbides and nitrides and the values of $1/2N_{xz}$ (or $1/2N_{yz}$) and /or $1/2N_{xy}$.

○: 560°C; ●: 600°C

and of the $d_{x^2-y^2}$ and d_{z^2} orbitals at the doubly-degenerate levels (denoted as $1/2N_{x^2-y^2}$ and $1/2N_{z^2}$ respectively), together with the bond populations of the M–C and M–N. Bearing in mind the connection between the catalytic activity and the degree of incompleteness of the d-electron subshells in the dehydrogenation reactions,[4] the correlation between the activity and the values of $1/2N_{xz}$ (or $1/2N_{yz}$) and/or $1/2N_{xy}$ seems significant.[5] As can be seen from Fig. 3, there is a linear dependence between the k values and the above-mentioned populations of MC (M=Ti, V, Nb, Hf, and Ta); it can be concluded that the transition-metal carbides thus catalyze the dehydrogenation of ethylbenzene as an electron acceptor.

Finally, it is worthy of emphasis, on the basis of the above consideration, that the transition-metal nitrides are not less active than the carbides thereof and that the catalytic activity follows the order: NbN$\gtrsim$ZrN$>$VN$\gtrsim$HfN$\gtrsim$CrN.

We wish to express our appreciation to the Data Processing Center of Kyushu University for the generous permission to use the FACOM 230-60 computer.

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[4] S. Z. Roignskii, *Zh. Fiz. Khim.*, **5**, 249 (1935).

[5] An increase in the formal charge of M, which is almost directly related to the sum of net orbital populations of the d_{x^2}, d_{yz}, d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals at triply- and doubly-degenerate levels, does not always give a high catalytic activity (see Fig. 1); the relatively large values of $^1/_2N_{x^2-y^2}$ and/or $^1/_2N_{z^2}$ of such nitrides as ZrN and HfN diminish the values of $^1/_2N_{xz}$ (or $^1/_2N_{yz}$) and/or $^1/_2N_{xy}$ in spite of their large formal charges of M (+3.494 and +3.157 for Zr and Hf respectively). The net orbital populations of the d_{xz}, d_{yz}, and d_{xy} orbitals at the LU degenerate levels seem more significant than the formal charge of transition metal.