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RESEARCH NOTE

Two-Step Methane Conversion to Higher Hydrocarbons: Comment on the Relevance of Metal–Carbon Bond Strength

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Herein, data available in the literature for nonoxidative, two-step CH_4 homologation over SiO_2-supported transition metals are analyzed according to the principle of Sabatier. Volcano plots are constructed which provide empirical evidence to support the hypothesis that the metal–carbon bond strength is pivotal to determine catalyst efficiency, chain-growth probability, and selectivity to C_2^+ hydrocarbons.

INTRODUCTION

The dependence on oil this century (1) is expected to be gradually offset in the next century by an increasing dependence on natural gas (2). Thus, it has been of considerable interest to convert natural gas into more commercially useful chemicals (3, 4). Direct CH_4 conversion into other chemicals such as synthesis gas (5) or C_2^+ hydrocarbons (3) is typically undertaken at relatively high temperatures. However, two independent reports in 1991 concerning the two-step nonoxidative conversion of CH_4 to C_2^+ alkanes over reduced Group VIII transition metals addressed the possibility of an indirect conversion route at temperatures lower than 773 K (6, 7). Two steps were utilized to circumvent the inherent thermodynamic limitation in the direct, low-temperature conversion of CH_4 to C_2^+ hydrocarbons. Since that time, there have been numerous investigations of this two-step route to CH_4 homologation by researchers at the Université de Nancy (8–16), Eindhoven University of Technology (17–19), and elsewhere (20–34). During the first step the catalyst is exposed to CH_4, in which both dissociative adsorption and some C–C bond formation occur (35, 36). Hydrogen is subsequently introduced in the second step to hydrogenate the surface carbonaceous deposits and induce alkane desorption, though hydrogenolysis reactions can also occur (36). Although the overall process is not truly catalytic (9), the individual heterogeneous reactions involved (dissociative adsorption, C–C bond formation, hydrogenation, hydrogenolysis, and desorption) are fundamental to catalysis.

Regarding this two-step process for CH_4 conversion, the importance of the metal–carbon bond strength ($Q_{\text{M-C}}$) has been emphasized by van Santen and co-workers (17–19). They discussed that $Q_{\text{M-C}}$ is pivotal to determine the type of carbonaceous deposit, the amount which is hydrogenated during the second step, and the balance between carbon–carbon bond formation and methanation during the second step (17–19). Herein, experimental data taken from the work of van Santen and co-workers (17–19) are combined with data obtained from Shustorovich and Benziger (37, 38) to construct volcano plots which illustrate the aforementioned phenomena.

RESULTS AND DISCUSSION

In the early 1990s, Koerts *et al.* investigated the nonoxidative, two-step homologation of CH_4 over SiO_2-supported Group VIII transition metals (19); a summary of their data is provided in Table 1. The catalyst metal (M) contents (μmol M/g_{cat}) were estimated from apparent nominal weight loadings; however, it is unclear in reference (19) as to whether or not the metal loadings are nominal or analytical. Thus, if these are nominal values and the metal salts used for catalyst preparation were not completely anhydrous, there may exist uncertainty in the values for metal content in Table 1. Metal dispersions (D) were measured by CO chemisorption (19). The reduced metal surface concentration (μmol $M_{\text{surf}}/g_{\text{cat}}$) was thus directly estimated from the total metal content and the dispersion. The amounts of surface carbon hydrogenated at 368 K (μmol C$/g_{\text{cat}}$) were estimated from the data in reference (19) by assuming that *m*mol in Table 1 of reference (19) are actually μmol. If this were not the case, then the estimated atomic ratios of surface carbon hydrogenated to reduced surface metal atoms (C$/M_{\text{surf}}$) shown in Table 1 herein would have to be multipled by a factor of 1000 and thus would greatly

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TABLE 1

Experimental CH_4 Homologation Data Obtained from Koerts *et al.* (19) (Reaction Conditions: CH_4 Adsorption at 733 K, H_2 Introduction at 368 K)

Catalyst	μmol M/g_{cat}	D (%)[a]	μmol M_{surf}/g_{cat}	μmol C/g_{cat}[b]	μmol C/M_{surf}	Sel. to CH_4 (%)
10% Co/SiO_2	1697	2.2	37.3	26.7	0.72	79.6
5% Ru/SiO_2	495	35	173	23.7	0.14	80.5
10% Ni/SiO_2	1704	13	222	56	0.25	89.3
3% Rh/SiO_2	292	55	161	11.3	0.07	95.8
4% Pt/SiO_2	205	100[c]	205	1.8	0.009	89.7
5% Re/SiO_2	268	6.4	17.2	3.2	0.19	91.3
4% Ir/SiO_2	208	30	62.4	3.2	0.05	98.4

[a] Dispersion measured by CO chemisorption.

[b] The amount of carbon hydrogenated at 368 K. It is assumed that mmol in Table 1 of Koerts *et al.* (19) are actually μmol.

[c] A value of 100% for Pt dispersion is used rather than 104% (19) for physical consistency.

exceed unity. In either case, however, the qualitative empirical trends developed herein would be unaffected. The selectivities to CH_4 during hydrogenation listed in Table 1 are taken directly from Koerts *et al.* (19).

It is worth mentioning that the estimated C/M_{surf} values shown in Table 1 herein are consistent with early data reported by Belgued *et al.* (8). Optimal temperatures for carbon hydrogenation (T_2) over supported Ru, where optimal is defined as the temperature which maximizes the amount of homologated CH_4, are compared in Table 2 with data from Table 1 as a function of CH_4 adsorption temperature (T_1). The data indicate that as T_1 increases above 473 K the amount of homologated CH_4 over Ru concomitantly decreases. In addition, it is reasonable to expect that as T_2 decreases below 393 K the amount of homologated CH_4 over Ru concomitantly decreases. The data reported by Koerts *et al.* (19) were obtained at $T_1 = 733$ K and $T_2 = 368$ K and are quantitatively consistent with these expectations, as shown in Table 2. It should also be noted that these C/Ru_{surf} values were calculated from data obtained under different experimental conditions (8, 19); i.e., these values are also a function of gas space velocity, partial pressure, and exposure duration (13–16).

In general, it may be stated that the CH_x species formed during dissociative CH_4 adsorption are a function of metal, metal structure, support, metal–support interactions, and system variables (such as residence time, temperature, and pressure). For example, when CH_4 dissociatively adsorbs on a reduced transition metal surface, it involves a concomitant σ donation from CH_4 to the surface and a back-donation from the metal surface to CH_4 (39, 40). The resultant CH_x surface fragment typically occupies an adsorption site which completes its tetravalency (39). As a consequence of these electronic and geometric constraints, the formation of CH_x species via CH_4 dissociation is in many cases structure sensitive (39). The data for two-step CH_4 homologation analyzed and discussed herein were obtained for SiO_2-supported metals; therefore, it is assumed herein that support effects and metal–support interactions are negligible for these data. Due to the wide range of metal dispersions and degrees of reduction for the supported metals used by Koerts *et al.* (19), it is not possible to further elucidate the influence of metal particle size or structure in the absence of additional information. Thus, this aspect is not further discussed herein. All catalysts in their study were subject to CH_4 exposure under identical experimental conditions; thus, this issue can be ignored herein. In addition, Koerts *et al.* were not able to detect any C–H vibrations on the catalyst surfaces during CH_4 adsorption at or above 723 K (19), indicating that the surface carbon species were severely hydrogen deficient under their conditions. Thus, focusing on metal–carbon interactions as a key independent variable seems reasonable for the purposes of the comparative, empirical study herein.

TABLE 2

A Comparison of CH_4 Homologation Data Reported by Belgued *et al.* (8) and Koerts *et al.* (19)

T_1 (K)	T_2 (K)	C/Ru_{surf}	Reference
473	393	1.00	(8)
513	433	0.99	(8)
553	433	0.85	(8)
593	433	0.41	(8)
733	368	0.14	Table 1

In this regard, three main types of carbon deposits have been observed during dissociative CH_4 adsorption on Group VIII transition metals, i.e., carbidic, amorphous, and graphitic (12, 19). The carbidic species is most likely adsorbed in an atomic state at 3-fold or 4-fold hollow sites and has only metal atoms in its first coordination shell (12, 19, 41); presumably this reactive carbon species is selective to C_2^+ formation upon hydrogenation (12, 19). As mentioned previously, some C–C bond formation can occur during dissociative CH_4 adsorption; consequently, it is possible that some of the C_2^+ species evolved during the hydrogenation step form prior to introduction of H_2. However, the qualitative trend in adsorption energies for small hydrocarbon fragments on transition metal surfaces, within the BOC-MP formalism, essentially parallels that of atomic carbon (37). For example, the estimated heats of adsorption for atomic carbon on Fe/W (200 kcal/mol), Ni (171 kcal/mol), and Pt (150 kcal/mol) surfaces are qualitatively proportional to the heats of adsorption of $H_3C–C$ (141, 115, and 97 kcal/mol, respectively) and $H_2C{=}CH$ (71, 55, and 44 kcal/mol, respectively). Consequently, heats of adsorption for atomic carbon may well be representative of, at least on a relative basis, the activity and selectivity of different metal surfaces for the activation of CH_4 and the formation of adsorbed C and C_2^+ species. Therefore, estimated values of the metal–carbon bond strength, $Q_{\text{M-C}}$, are used herein as the independent correlating variable.

A summary of $Q_{\text{M-C}}$ values estimated by Benziger (38) is provided in Table 3. Although "subjective judgment was used to weight" these data (38), the correlations provided herein at least provide some implicit credence to their approximate validity. The C_2^+ hydrocarbon species produced during hydrogenation may (12) or may not (19) conform to an Anderson–Schultz–Flory distribution; regardless, chain-growth probabilities for carbon–carbon bond formation (α) are provided in Table 3 for comparative purposes.

In terms of catalyst efficiency for nonoxidative, two-step CH_4 homologation, it is desirable to maximize the product yield, i.e., the amount of carbon which is "recoverable" by hydrogenation, relative to the total amount of carbon deposited during CH_4 adsorption. In the absence of the latter data in reference (19), the atomic ratio of "recoverable" carbon, relative to the reduced metal surface (C/M_{surf}), is used herein as a measure of catalyst efficiency. From a practical perspective, this value is also of importance. Regardless, a plot of C/M_{surf} (Table 1) versus $Q_{\text{M-C}}$ (Table 3) demonstrates a volcano-type plot with Co at the apparent maximum, as shown in Fig. 1. Granted the possible uncertainty in the estimates for both C/M_{surf} and $Q_{\text{M-C}}$, this correlation

TABLE 3

Atomic Carbon Heats of Adsorption ($Q_{\text{M-C}}$) and Chain-Growth Probabilities (α_1, α_2) for Transition Metals

Metal	$Q_{\text{M-C}}$ (kcal/mol)[a]	α_1[b]	α_2[c]
W	260	—	0
Mo	183	—	0
Fe	166	0	0
Cu	135	0	0
Au	50	0	—
Ru	140	0.15	0.14 ± 0.04
Rh	130	0.02	0.018 ± 0.004
Pd	130	0	0
Ni	169	0.09	0.18 ± 0.13
Co	162	0.20	0.22 ± 0.14
Re	180	—	0.032 ± 0.014
Pt	130	—	0.028 ± 0.028
Ir	130	—	0.0035 ± 0.0035

[a] Reference (38).

[b] Reference (7).

[c] Data are a numerical average of the probability for carbon-carbon bond formation from two adsorbed C_1 surface fragments and for insertion of CH_x species into a hydrocarbon chain (19).

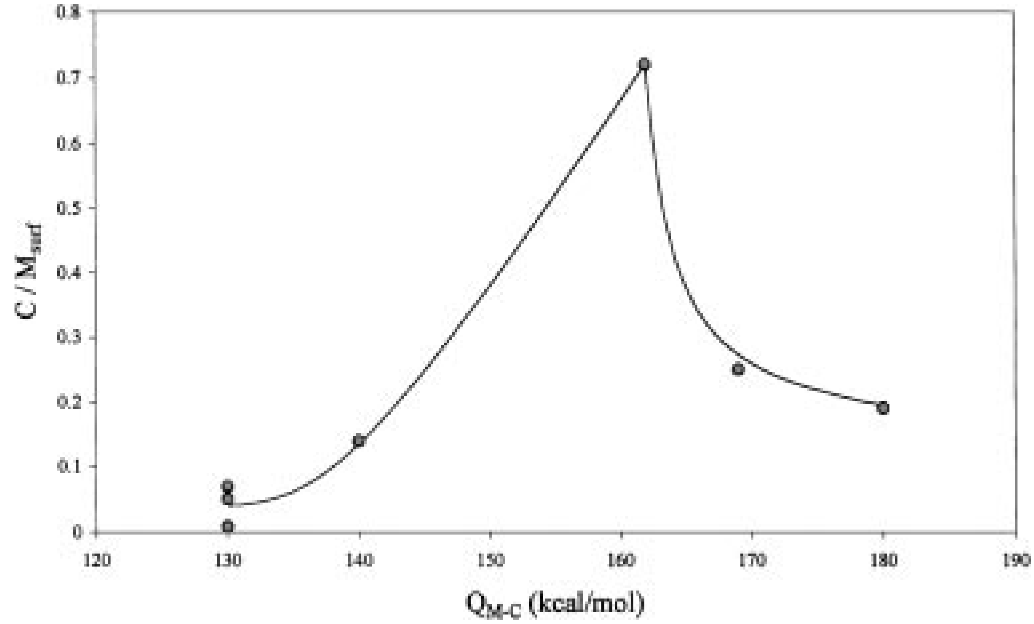

FIG. 1. Atomic ratio of carbon hydrogenated to reduced metal surface atoms (C/M_{surf}) as a function of atomic carbon heat of adsorption ($Q_{\text{M-C}}$). The solid line is an empirical "guide to the eye." See Table 1 for details.

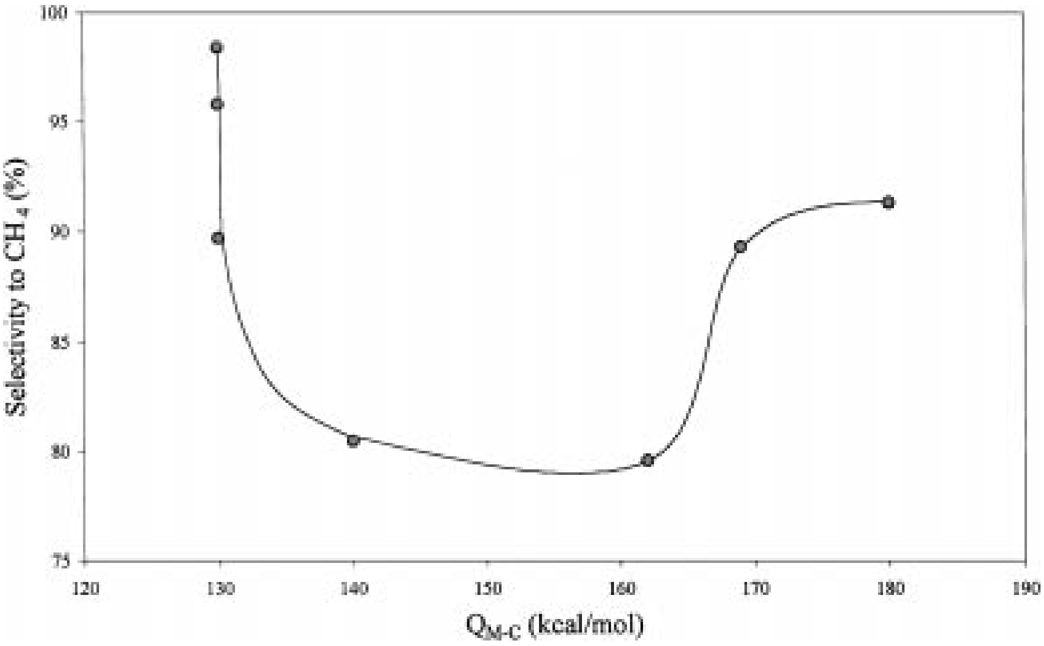

FIG. 2. Selectivity during hydrogenation to CH_4 as a function of atomic carbon heat of adsorption ($Q_{\text{M-C}}$). The solid line is an empirical "guide to the eye." See Table 1 for details.

is rather interesting. If physically valid it indicates that the most efficient metals for CH_4 homologation, at least under the experimental conditions chosen by Koerts *et al.* (19), exhibit metal–carbon bond strengths on the order of 140 to 169 kcal/mol.

Maximization of C_2^+ hydrocarbon yield obviously requires a minimization of hydrogenation to CH_4 during the second step of the homologation process. A plot of selectivity to CH_4 during hydrogenation (Table 1) versus $Q_{\text{M-C}}$ (Table 3) yields an inverse volcano-type plot with a broad

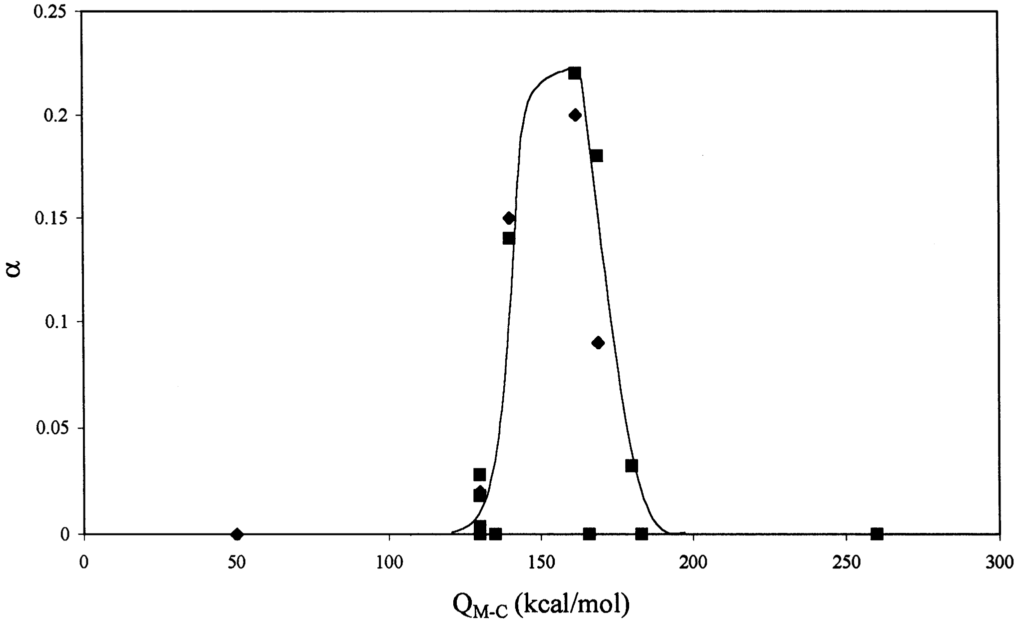

FIG. 3. Chain growth probability (α) during two-step CH_4 homologation as a function of atomic carbon heat of adsorption ($Q_{\text{M-C}}$). The solid line is an empirical "guide to the eye." Data are obtained from (■) reference (19) and (◆) reference (7). See Table 3 for details.

minimum for metal–carbon bond strengths on the order of 140 to 162 kcal/mol, as shown in Fig. 2. A plot of chain growth probability (α) versus $Q_{\text{M-C}}$ (Table 3) also yields a volcano-type plot with a maximum in a similar range of metal–carbon bond energies, as shown in Fig. 3. An apparent discrepancy in Fig. 3 arises for Fe, which exhibits a zero α value although its estimated metal–carbon bond strength lies close to the curve maximum. Although it is reasonable to disregard this apparent discrepancy when considering the inherent uncertainty in such an empirical correlation, there is a plausible explanation. Simply, if $Q_{\text{Fe-C}}$ is significantly greater than $Q_{\text{Ni-C}}$, as suggested by Koerts *et al.* (7), then the estimated value for $Q_{\text{Fe-C}}$ in Table 3 and Fig. 3 is too low. Use of a higher $Q_{\text{Fe-C}}$ value could thus remove the apparent discrepancy. Nevertheless, if the preceding analysis is physically valid, optimal choices of metal for two-step CH_4 homologation would be restricted to Ru, Os, and Co. Apparently, Os has not yet been studied for low-temperature, two-step, nonoxidative CH_4 homologation; therefore, the predicted applicability of this metal awaits experimental confirmation or rejection. It is necessary to clarify that the conclusion that Ru, Os, and Co are the preferred metals for CH_4 homologation is not necessarily valid for multimetallic catalysts or experimental conditions which differ from those of Koerts *et al.* (19). Nevertheless, it does provide some physical basis for the investigation of bimetallic Co–Pt (23), Co–Ru (26), and Co–Cu (32) catalysts.

SUMMARY

In this Research Note, the relevance of the metal–carbon bond strength on catalyst performance for CH_4 homologation has been addressed via correlation of experimental (19) and empirical (37, 38) data. Specifically, it has been shown that catalyst efficiency, selectivity to CH_4, and chain growth probability correlate well with estimates of heats of adsorption for atomic carbon on reduced metal surfaces. A caveat, however, is that these volcano-type correlations are likely a strong function of several factors, such as the operating conditions and the support. For example, similar volcano-type correlations for CO_2–CH_4 reforming demonstrate a strong dependence on the support (42). Nevertheless, volcano-type correlations such as those described herein are inherently useful in that they can assist in the development of a more coherent conceptual picture of a process. Possibly, over time, correlations such as these can bring researchers closer to "Butt's Vision," i.e., "toward the a priori determination of catalytic properties" (43).

END NOTE

"Now, as to myself, I have so described these matters as I have found them and read them; but if anyone is inclined to another opinion about them, let him enjoy his sentiments without any blame from me" (44).

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