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The role of metal–support interactions in CO_2 reforming of CH_4

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Abstract

Prior investigations of CO_2 reforming of CH_4 have indicated that when TiO_2 is used as a support, TiO_x species formed during reduction decorate the metal particle surfaces, thereby geometrically destroying large ensembles of metal atoms necessary for carbon deposition. In addition, it has been suggested that sites at the metal–TiO_x interface are created which promote catalyst activity. To further elucidate the role of metal–support interactions, CO_2 reforming of CH_4 has been investigated over a series of SiO_2- and TiO_2-supported transition metals. Turnover frequencies for CO formation were found to depend on both the support and the %-d character of the metal. In situ DRIFT spectra of CH_4 and CO_2 adsorption indicate that oxygen from the support can participate in the activation of both CH_4 and CO_2, and that CH_xO species can be formed during CH_4 adsorption on TiO_2-supported transition metals after reduction in H_2 at 773 K.

Keywords: Methane; Carbon dioxide reforming; Titania; Metal–support interactions

1. Introduction

Prior investigations of CO_2 reforming of CH_4 over supported Ni [1], Rh [2,3], Pd [4], Ir [5] and Pt [6] catalysts have indicated that metal–support interactions (MSI) can affect both catalyst activity and activity maintenance. For example, it has been shown that TiO_2-supported Group VIII metals exhibit suppressed carbon formation during CO_2–CH_4 reforming [1–6], presumably due to the decoration of metal particle surfaces by TiO_x species which destroy large ensembles of metal atoms that serve as active sites for carbon deposition [1,6]. In addition, it has been proposed that sites in the metal–support interfacial region may promote catalyst activity [1,7]. Through the use of model TiO_x/Pt catalysts, evidence to support these hypotheses has recently been obtained [8].

In the present study to further elucidate the role of MSI, CO_2 reforming of CH_4 has been investigated over a series of SiO_2- and TiO_2-supported transition metals. The dependence of catalyst activity on the support as well as the %-d character of the metal was determined. In situ DRIFT spectra obtained during CH_4 and CO_2 adsorption revealed that oxygen from the support can react with these two molecules and that CH_xO species are formed during CH_4 adsorption on TiO_2-supported transition metals, presumably in the metal–titania interfacial region. These results are described in this paper.

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2. Experimental

With the exception of Rh/SiO_2, which was prepared via an incipient wetness technique by impregnating SiO_2 obtained from Alpha Products (330 m^2/g) with $Rh(NO_3)_3 \cdot 2H_2O$ [9], the catalysts were prepared via incipient wetness by impregnating either SiO_2 (Davison Grade 57, 271 m^2/g), or TiO_2 (Degussa P-25, 47 m^2/g) with the following metal–salt precursors: $Cu(NO_3)_2 \cdot xH_2O$ (Aldrich), $Co(NO_3)_2 \cdot xH_2O$ (Aldrich), $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich), $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich), $RuCl_3 \cdot xH_2O$ (Aldrich), $RhCl_3 \cdot xH_2O$ (Alpha Aesar), $PdCl_2$ (Alfa Aesar), $IrCl_3 \cdot 3H_2O$ (Alfa Aesar), and $H_2PtCl_6 \cdot H_2O$ (Aldrich). SiO_2-supported Ir, Ru, Co and Cu catalysts were neither prepared nor studied. Pure SiO_2 (Davison Grade 57) and TiO_2 (Degussa P-25) were also studied as references. All catalysts were dried in air at 423 K overnight and subsequently sieved to a 120/70 mesh fraction (0.12–0.20 mm) prior to use. With the exception of Rh/SiO_2, catalyst pretreatment consisted of heating in 12 sccm H_2 (WHSV=14 400–180 000 $cm^3/g/h$) for 30 min at 423 K, followed by heating to 773 K and reducing in flowing H_2 for 60 min. The Rh/SiO_2 catalyst was reduced in diluted H_2 ($H_2/He=1/4$) for 2 h at 773 K. After cooling the catalyst in flowing H_2 to 723 K, the catalyst was purged with flowing He (WHSV=43 200–540 000 $cm^3/g/h$) for 30–60 min to remove adsorbed hydrogen from the surface. After reduction at 773 K, H_2 and CO chemisorption were measured on all catalysts at 300 K using a stainless steel volumetric apparatus to determine metal dispersion via application of the dual isotherm method [10]. Because reduction of TiO_2-supported metals at 773 K is known to induce an MSI state [11], additional isotherms at 300 K were also obtained after reduction to 473 K to better estimate metal dispersion in these catalysts. Metal loading was quantified by either inductively coupled plasma spectrophotometry (ICPS) or neutron activation analysis (NAA).

A high temperature reactor system described previously [1] was utilized to determine catalyst activity. The amount of catalyst used during these experiments was varied between 4 and 50 mg to probe the influence of the reverse reaction and to maintain differential conditions. Typical activity tests were carried out under ca. 740 Torr absolute pressure, with a feed composition of $CO_2/CH_4/He=1/1/1.8$ and a total feed flow rate of 20 sccm (WHSV=24 000–300 000 $cm^3/h/g$) over a temperature range of 673–723 K. An N_2-purged FTIR spectrometer (Mattson Instruments, RS-10 000) equipped with a DRIFTS (Diffuse reflectance infrared fourier transform spectroscopy) cell (Harrick Scientific, HVC-DR2) and a praying mantis mirror assembly (Harrick Scientific, DRA-2C0) was used to study CH_4 and CO_2 adsorption between 293 and 773 K. These experiments were carried out after in situ reduction at 773 K under ca. 740 Torr absolute pressure with a feed composition of either $CH_4/Ar=1/4$ or $CO_2/Ar=1/4$ and a total flow rate of 5 sccm (WHSV=4000–12 000 $cm^3/h/g$). All spectra were obtained in situ and are represented as an average of 1000 scans from 750 to 4000 cm^{-1} with a resolution of 4 cm^{-1} in the presence of the gas-phase species; however, the bands for gas-phase CO_2 and CH_4 have been subtracted from the spectra for clarity. Absorbance plots are used so that peak losses as well as enhancements can be detected.

3. Results and discussion

While the dispersions of the SiO_2-supported metals were low, ranging from 2% to 26% (Table 1), the apparent metal dispersions of the TiO_2 catalysts, as indicated by the H/M or CO/M ratios, varied considerably (Table 2). In the case of Cu/TiO_2, both H_2 and CO are expected to adsorb weakly [12]; consequently, the number of Cu surface atoms determined with these probe molecules underestimates the true metallic Cu surface area. In fact, CO adsorbs more strongly on Cu^{+1} than Cu^0 [13]; therefore, the irreversible CO adsorption on the Cu/TiO_2 catalyst given in Table 2 may actually better estimate the number of Cu^{+1} sites. Nevertheless, considering the low Cu loading in this catalyst, it is not unreasonable to assume that the Cu is well dispersed [14,15]. The very high CO uptakes and noticeably lower H_2 uptakes measured for TiO_2-supported Ir, Ru and Rh after reduction at 473 K are reproducible, and they may be due to a combination of high metal dispersion, carbonyl cluster formation, and interaction with Cl impurities originating from the salt precursors. On TiO_2-supported Pt, Pd, Ir, Ru and Rh, the uptakes of both H_2 and CO are substantially reduced after reduction for 1 h at 773 K, as shown in Table 2. This

Table 1
Initial activity of SiO_2-supported metals for CO_2 reforming of CH_4 at 723 K

Catalyst	T_r (K)	Uptake$_{irr}$ (μmol/g$_{cat}$)		Dispersion[a] (%)		Conversion (%)		Initial activity		
		H_2	CO	H_2	CO	CH_4	CO_2	(μmol CO/s g$_{cat}$)	TOF–CO (s^{-1}) [b]	TOF–CH_4 (s^{-1}) [b]
SiO_2	773	0	0	–	–	0.05	0.1	0.12	[0.0004] [c]	[0.0001] [c]
5.8% Fe/SiO_2	773	–	10.5	–	2	0.1	0.2	0.27	0.03	0.01
6.8% Ni/SiO_2	773	96.7	184	17	16	2.9	6.5	66.9	0.35±0.01	0.11
0.8% Pt/SiO_2	773	4.7[d]	10.6	23	26	1.9	3.4	8.8	0.88±0.05	0.32
1.1% Pd/SiO_2	773	8.7	17.1	16	16	1.7	2.5	6.4	0.37±0.01	0.15
3.8% Rh/SiO_2	773	16.4	30.7	9	8	0.28	0.39	5.4	0.17±0.01	0.07

[a] Assuming H/M=CO/M=1/1 except for Fe, i.e., CO/Fe=1/2 [24].
[b] TOF based on the average number of surface atoms from both H_2 and CO adsorption.
[c] Units of μmol/s m^2.
[d] Total H_2 uptake.

Table 2
Initial activity of TiO_2-supported metals for CO_2 reforming of CH_4 at 723 K

Catalyst	%-d Character	T_r (K)	Uptake$_{irr}$ (μmol/g$_{cat}$)		H/M	CO/M	Conversion (%)		Initial activity		
			H_2	CO			CH_4	CO_2	(μmol CO/s g$_{cat}$)	TOF–CO (s^{-1}) [a]	TOF–CH_4 (s^{-1})
TiO_2	–	773	0	0	–	–	0.1	0.2	0.21	[0.0045] [b]	[0.0015] [b]
0.5% Cu/TiO_2	36	773	0.1	2.0	–	–	0.05	0.1	0.2	≤0.1	≤0.03
0.7% Co/TiO_2	39.5	773	0.4	4.0	0.007	0.067	0.1	0.2	0.5	0.1	0.03
0.8% Fe/TiO_2	39.7	773	0.0	7.9	–	0.105	0.15	0.3	0.7	0.1	0.03
1.2% Ni/TiO_2	40	773	2.4	17.5	0.023	0.084	3.2	5.9	30.2	1.7	0.60
0.8% Pt/TiO_2	44	773	0	5.3	0	0.12	6.0	10.8	26.0	4.9	1.70
		473	15.9[c]	23.1	0.75	0.55	–	–	–	1.1	0.39
0.4% Pd/TiO_2	46	773	3.8	7.0	0.21	0.19	3.3	6.9	15.5	2.2	0.71
		473	7.5	16.2	0.41	0.44	–	–	–	0.96	0.31
0.4% Ir/TiO_2	49	773	0.5	0.7	0.048	0.034	3.2	6.6	14.8	21	6.8
		473	16.3	46.5	1.6	2.2	–	–	–	0.70	0.23
0.5% Ru/TiO_2	50	773	1.3	26.6	0.051	0.51	7.4	12.2	197	7.4	2.8
		473	3.0	107	0.11	3.9	–	–	–	3.8	1.4
0.3% Rh/TiO_2	50	773	0.7	7.1	0.048	0.26	7.1	12.3	186	26	9.5
		473	7.3	115	0.54	8.5	—	–	–	6.8	2.5

[a] TOF based on surface metal atoms by CO adsorption.
[b] Units of μmol/s m^2.
[c] Total H_2 uptake.

behavior is routinely observed and is due to physical blockage caused by the presence of TiO_x suboxide species on the metal surfaces [1,6,11].

DRIFT spectra of TiO_2 and TiO_2-supported metals after reduction for 1 h at 773 K, when referenced to the spectrum of each corresponding catalyst after only 5 min under H_2 at 773 K, clearly show losses near 3660 cm^{-1} due to removal of hydroxyl groups on the titania [16] as well as strong losses between 910 and 960 cm^{-1} which are indicative of Ti–O bond cleavage

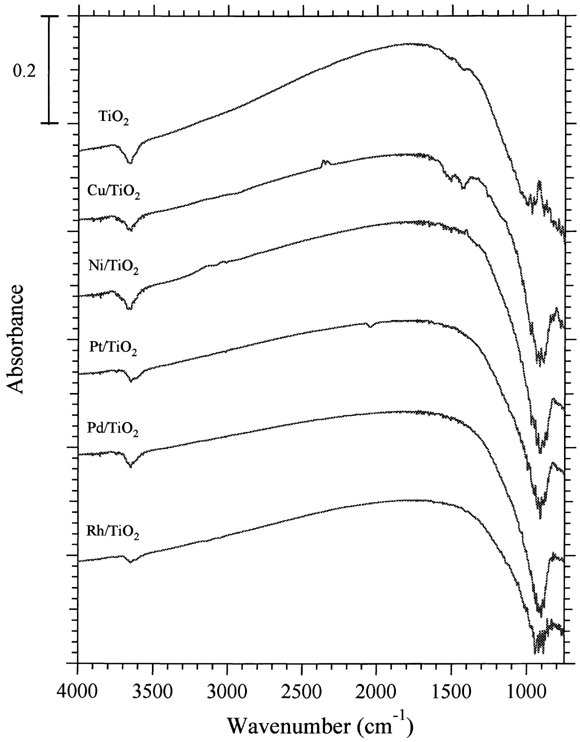

Fig. 1. DRIFT spectra of TiO_2 and TiO_2-supported metals after reduction for 1 h at 773 K, obtained in reference to the spectra of the catalysts after only 5 min of reduction at 773 K. Conditions: $H_2/Ar=5/4$ and $P_{tot}\approx740$ Torr.

and TiO_x formation [17], as shown in Fig. 1. XRD spectra of the as-prepared and reduced TiO_2-supported catalysts do not differ; therefore, the reduction of TiO_2 evidenced by DRIFTS is most certainly a surface-related phenomenon.

Neither SiO_2 nor TiO_2 showed appreciable activity for CO_2–CH_4 reforming at 723 K, as shown in Tables 1 and 2; however, TiO_2 is more active than SiO_2 on either a mass or surface area basis. As CO_2 reforming of CH_4 over metal oxides may proceed via a Mars-van Krevelen-type mechanism [18,19], the differences in activities may be related to the differences in the metal–oxygen bond strengths [20].

The initial specific activities (µmol/s g_{cat}) and turnover frequencies (s^{-1}) for CO_2 reforming of CH_4 at 723 K over SiO_2- and TiO_2-supported transition metals are shown in Tables 1 and 2, respectively. Observed CO_2 conversions were consistently higher than those of CH_4 due to the influence of the reverse water-gas shift reaction, in which H_2 produced via reforming reacts with CO_2 to yield H_2O and CO. Under these conditions, $H_2/CO \cong (3-w)/(1+w)$, where w equals the ratio of CO_2 conversion to CH_4 conversion. Time-on-stream data indicate that carbon formation reactions such as CH_4 decomposition and CO disproportionation are not expected to significantly alter the initial catalyst activities [1,6,20]. The roles of the reverse water-gas shift and carbon formation reactions are discussed in greater detail elsewhere [1,6,20]. It is of interest to note that at 723 K, the specific activities for supported Cu, Co and Fe are only slightly higher than those of the pure supports alone. It has been shown previously that SiO_2-supported Ni [1] and Pt [6] deactivate with time-on-stream due to extensive carbon formation. In addition, for TiO_2-supported transition metals, due to the possible mobility of TiO_x species on the metal surface under these reaction conditions, the state of the metal surface immediately after reduction may not be identical to the metal surface under reaction conditions. Therefore, to minimize complications in data interpretation, for all catalysts initial turnover frequencies are reported whose initial activity refers to the maximum catalyst activity observed during the initial 30 min on stream at 723 K.

Initial catalyst TOFs at 723 K were also examined as a function of the weight hourly space velocity (WHSV) by varying the catalyst mass, as shown for Rh/SiO_2 and Ni/TiO_2 in Fig. 2. The difference in observed trends between the two catalysts, which have a similar sieve fraction, indicates that the variation in TOF with WHSV is not due to external mass-transfer resistance, and Weisz criterion [21] calculations indicate that the observed variation in TOF with WHSV for Ni/TiO_2, and other catalysts, is not due to internal mass-transfer limitations. Gesser et al. [22] have shown during their investigation of CO_2–CH_4 reforming over a W wire that the influence of the reverse water-gas shift reaction diminishes with increasing space velocity. Further analysis of our data has indicated that the relationship with WHSV shown in Fig. 2 is almost certainly due to the influence of the reverse reaction, i.e., the hydrogenation of CO to CH_4, which becomes increasingly significant as the CH_4 conversion approaches that expected at thermodynamic equilibrium. If the observed *net* TOF for CO_2 reforming of CH_4 at 723 K, TOF_{CO}, is influenced

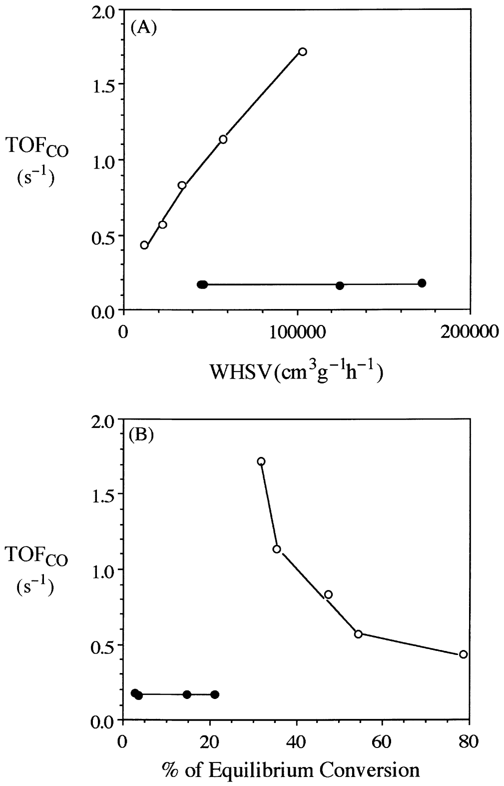

Fig. 2. TOF for CO formation at 723 K as a function of (A) WHSV and (B) percent of equilibrium conversion for (○) Ni/TiO_2 and (●) Rh/SiO_2. Reaction conditions: $P_{tot}\approx740$ Torr and $CH_4/CO_2/He=1/1/1.8$.

by the hydrogenation of CO to CH_4, then it can be approximated by the following expression:

$$TOF_{CO} = TOF_{for} - TOF_{rev}, \tag{1}$$

where TOF_{for} is the forward TOF for CO_2–CH_4 reforming and TOF_{rev} is the reverse TOF for the hydrogenation of CO to CH_4. If a general power rate law is assumed for the hydrogenation of CO to CH_4:

$$TOF_{rev} = k_r P_{H_2}^{\gamma} P_{CO}^{\delta}, \tag{2}$$

where P_{H_2} and P_{CO} are the partial pressures of H_2 and CO, respectively, and k_r is the power law rate constant for CO hydrogenation to CH_4 at 723 K, then a plot of the initial values of TOF_{CO} at each WHSV versus $P_{H_2}^{\gamma}$ P_{CO}^{δ}should be linear, with the slope being equal to the value of $-k_r$ at 723 K. Using the values of $\gamma=0.9\pm0.1$ and $\delta=-0.3\pm0.1$ reported by Vannice [23] for Ni/TiO_2, the following relationship was found for CO_2 reforming of CH_4 over Ni/TiO_2:

$$TOF_{CO} = 2.01 - 0.28 P_{H_2}^{0.9} P_{CO}^{-0.3}. \tag{3}$$

Similar linear relationships were found for other catalysts, as shown in Table 3. Thus, it appears that the observed variation in catalyst activity with WHSV for CO_2 reforming of CH_4 is due in part to the reverse reaction, as suggested previously using a similar analysis [1]. Consequently, previous kinetic data reported in the literature for CO_2–CH_4 reforming which were obtained at low space velocities and near equilibrium conversions must be considered to be suspect. With the exception of TiO_2-supported Pt, Ru and Rh (see Table 2), all CH_4 and CO_2 conversions in Tables 1 and 2 are much lower than the respective equilibrium values of 10.1% and 16.1%. It has already been shown that under these reaction conditions the influence of the reverse reaction is negligible over Pt/TiO_2 [6]. In addition, analysis of kinetic data for TiO_2-supported Ru and Rh via the preceding equations illustrates that the maximum observed net TOFs,

Table 3
Analysis of TOF data for supported metal catalysts at 723 K

Catalyst	$TOF_{CO}=TOF_{for}-k_r P_{H_2}^{\gamma} P_{CO}^{\delta}$				TOF_{max}^{b}
	γ [a]	δ [a]	k_r (s^{-1} $Torr^{-(\gamma+\delta)}$)	TOF_{for} (s^{-1})	
Ni/SiO_2	0.8[c]	−0.3[c]	0.06	0.43	0.36
Ni/TiO_2	0.9	−0.3	0.28	2.01	1.73
Rh/TiO_2	1.7	−0.1	0.056	32.9	26.2
Ru/TiO_2	2.0	−0.5	0.026	9.1	7.4

[a] Data obtained from [23].
[b] Maximum TOF observed at highest space velocity.
[c] Values for Ni/Al_2O_3.

TOF_{max}, are very similar to the calculated TOFs for CO_2–CH_4 reforming in the absence of the reverse reaction, TOF_{for}, as shown in Table 3. Consequently, the data shown in Tables 1 and 2 are most likely in the kinetic regime and are not severely influenced by thermodynamic equilibrium.

From an electronic viewpoint, the activation of CH_4 on a metal surface involves interaction with both the HOMO and the LUMO of the metal [25]. An empirical measure of the electronic structure of a metal is Pauling's %-d character [26]; consequently, if CH_4 activation on the metal surface is rate-limiting during CO_2 reforming of CH_4, as suggested previously [1], then catalyst activity should depend on %-d character. Indeed, the TOF values for SiO_2-supported metals show a volcano-type correlation with %-d character, as shown in Fig. 3. The results of Mark and Maier [27] and Zhang et al. [3] indicate that CO_2 reforming of CH_4 is structure insensitive over noble metals with dispersions below about 25%, i.e., on larger crystallites; thus, as all SiO_2-supported catalysts studied in this investigation fit this criterion (see Table 1), it is reasonable to assume that the relationship shown in Fig. 3 is not affected by structure sensitivity. Furthermore, as the role of the SiO_2 support in the catalytic cycle should be minimal, this trend should represent behavior of the metal only.

Due to the presence of TiO_x species on the metal surface under reaction conditions, calculation of TOFs for the TiO_2-supported metals is more complicated than with the SiO_2-supported metals. Hence, TOFs were calculated based on the CO uptake after reduction at 473 K as well as that after reduction at 773 K to set both lower and upper limits to the TOFs, as given in Table 2. If CO/M ratios exceeded 1, a metal dispersion of unity was assumed. As shown in Fig. 4, TOFs for TiO_2-supported metals can be correlated with metal %-d character; however, a very different trend is obtained compared to that for SiO_2-supported metals. Although the reforming of CH_4 with CO_2 has been reported to be structure-sensitive over TiO_2- and Al_2O_3-supported Rh for dispersions above 25% [3]; establishing this unambiguously with SMSI catalysts involving TiO_2 is not easy because of the difficulty in accurately measuring metal crystallite size. Consequently, although this different trend for TiO_2-supported metals may possibly be affected by the high apparent metal dispersions of Ir, Ru and Rh, it is much more likely that the rate data reflect the participation of the TiO_2 support in the catalytic cycle.

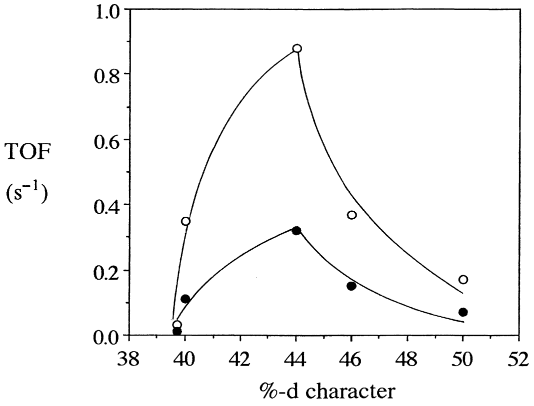

Fig. 3. Correlation of TOF for (●) CH_4 consumption and (○) CO formation during CO_2 reforming of CH_4 at 723 K with metal %-d character for SiO_2-supported metals. Reaction conditions: $P_{tot}\approx740$ Torr, $CH_4/CO_2/He=1/1/1.8$, and WHSV=24 000–300 000 $cm^3/g/h$. (The curves shown are meant only as a guide.)

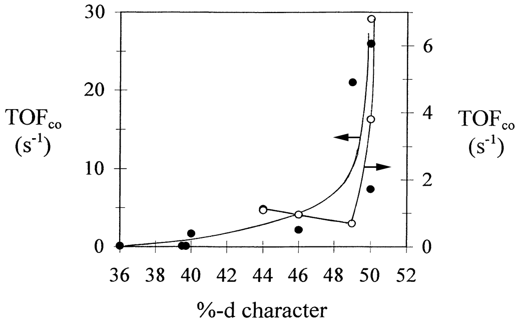

Fig. 4. Correlation of TOF for CO formation during CO_2 reforming of CH_4 at 723 K (TOF_{CO}) with metal %-d character for TiO_2-supported metals. TOF_{CO} values were calculated using metal dispersion determined after reduction at either 473 K (○) or 773 K (●). Reaction conditions: $P_{tot}\approx740$ Torr, $CH_4/CO_2/He=1/1/1.8$, and WHSV=24 000–300 000 $cm^3/g/h$. (The curves shown are meant only as a guide.)

The aforementioned results indicate that the specific activity for CO_2 reforming of CH_4 depends on both the metal electronic structure, represented by %-d character, and the support. To illustrate that such relationships can be more general, the turnover frequencies reported by Rostrup-Nielsen and Bak Hansen [28] for both CO_2 and H_2O reforming of CH_4 over metals dispersed on Al_2O_3-stabilized MgO are also plotted as a function of metal %-d character, as shown

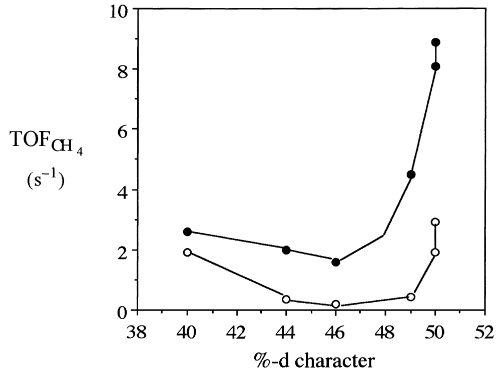

Fig. 5. Correlation of TOF for CH_4 consumption during CH_4 reforming at 823 K (TOF_{CH_4}) with metal %-d character for MgO-supported metals. (○) CO_2–CH_4 reforming. Reaction conditions: $P_{tot}\approx1$ atm, $CO_2/CH_4/H_2=10/2.5/1$, and WHSV=432 000–2 612 000 $cm^3/g/h$. (●) H_2O–CH_4 reforming. Reaction conditions: $P_{tot}\approx1$ atm, $H_2O/CH_4/H_2=10/2.5/1$, and WHSV=432 000–2 160 000 $cm^3/g/h$. All TOF data from Ref. [28]. (The curves shown are meant only as a guide.)

in Fig. 5. The observed trend is clearly different from that observed for SiO_2-supported metals (Fig. 3) and is much more similar to that obtained here with TiO_2-supported metals. These two latter relationships may indicate that MgO and TiO_2 play a role in the catalytic cycle.

DRIFT spectra of SiO_2 and SiO_2-supported transition metals after exposure to CH_4 at 293 K reveal a strong interaction with isolated silanols [29], as shown by the common loss at 3744±2 cm^{-1} in Fig. 6. Infrared evidence for the interaction of CD_4 with isolated hydroxyl groups on both SiO_2 and Al_2O_3 to form –OD groups has been reported previously [30,31]. In addition, as the CH_4 adsorption temperature increases, the interaction of CH_4 with isolated silanols does not significantly change, while the interaction of CH_4 with strained or broken siloxane bridges increases dramatically [32], as shown by the strong loss at about 1350 cm^{-1} in Fig. 7. For SiO_2-supported Ni, Rh and Pt, the interaction of CH_4 with hydroxyl groups and siloxane bridges led to the formation of adsorbed CO on the reduced metal surfaces [20]. This is consistent with the recent observation that the interaction of CH_4 with SiO_2- and Al_2O_3-supported Co, Ni, Ru, Rh, Ir and Pt leads to the formation of surface carbon, as well as gas-phase H_2 and CO at temperatures higher than 600 K [33]. Although it is possible that contamination by trace amounts of O_2, which has no dipole moment and is thus IR inactive, is the cause of this phenomenon, the observed interaction of CH_4 with both OH groups and siloxane bridges (Fig. 7) indicates that some oxygen is being supplied by the support.

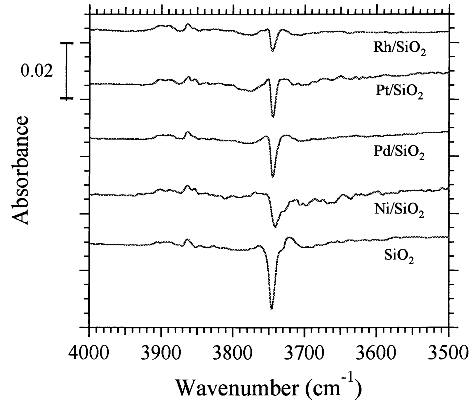

Fig. 6. DRIFT spectra of SiO_2 and SiO_2-supported Ni, Pd, Pt and Rh after exposure to CH_4 at 293 K, referenced to spectrum of the reduced catalyst prior to gas admission. Conditions: $P_{tot}\approx740$ Torr and $CH_4/Ar=1/4$.

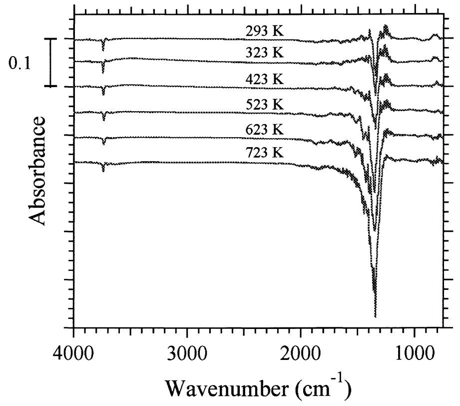

Fig. 7. DRIFT spectra of SiO_2 during exposure to CH_4 from 293 to 723 K, referenced to spectrum of the reduced catalyst prior to gas admission. Conditions: $P_{tot}\approx740$ Torr and $CH_4/Ar=1/4$.

DRIFT spectra of TiO_2 and TiO_2-supported transition metals after exposure to CH_4 at 423 K are shown in Fig. 8. The variation in the baseline of the spectra is attributed to further reduction of the titania by CH_4 upon dissociation and the subsequent introduction of hydrogen atoms [16,17]. It appears that the interaction of CH_4 with surface Ti–O species, indicated by the loss at 930±20 cm^{-1} [17], is accompanied by the

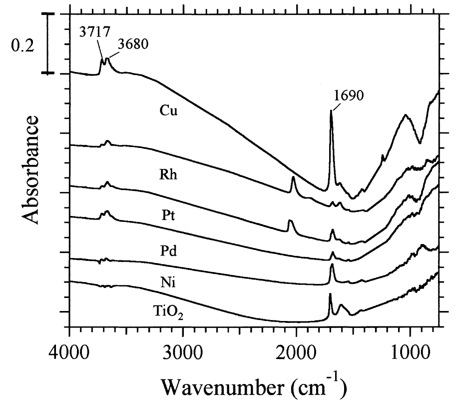

Fig. 8. DRIFT spectra of TiO_2 and TiO_2-supported Ni, Pd, Pt, Rh and Cu during exposure to CH_4 at 423 K, referenced to spectrum of the reduced catalyst prior to gas admission. Conditions: $P_{tot}\approx740$ Torr and $CH_4/Ar=1/4$.

formation of hydroxyl groups on both anatase (3717 and 3669 cm^{-1}) and rutile (3680 cm^{-1}), as shown in Fig. 8. A sharp band at 1690±10 cm^{-1}, indicative of $H_2C=O$ species strongly coordinated at Lewis acid (Ti^{+n}) sites [34], was observed on all catalysts independent of the degree of interaction with surface Ti–O species. In addition, adsorbed CO was identified on both Rh (2028 cm^{-1}) and Pt (2060 cm^{-1}), indicating that CH_4 had reacted with surface oxygen to form CO. The decreased intensity of the band at 1690 cm^{-1} on these two catalysts may indicate that $H_2C=O$ species are formed in the metal–support interfacial region and may be precursors to CO formation on the metal surface. In general, these DRIFTS results are consistent with an earlier report by Fancheng et al. [35] that CH_4 dissociation to CH_x and CH_xO species can readily occur on reduced titania surfaces.

DRIFT spectra after CO_2 adsorption at 293 K on TiO_2 and TiO_2-supported transition metals are shown in Fig. 9. Well-defined bands at 1588 and 1436 cm^{-1}, due to bicarbonate species, and weak bands at 1675 and 1223 cm^{-1}, due to bidentate carbonate species, are observed on all catalysts [34,36]. Although the bands present at 1540, 1380, and 1363 cm^{-1} on the Rh/TiO_2 catalyst were not observed during CO_2 adsorption on pure TiO_2, they are assigned to modes of surface formate species [36]. Observation of additional bands on Rh/TiO_2 at 2971, 2954 and 2871 cm^{-1} (not shown for brevity) confirms this assignment [20]. The presence of formate species during CO_2 adsorption, and thus the creation of C–H bonds, indicates that hydrogen atoms remain on the titania surface after reduction and purging at 723 K. This is consistent with the NMR identification of $(Ti\text{–}H)^{+3}$ species after reduction of Rh/TiO_2 at 773 K [37], as well as recent hydrogen TPD results with reduced Pt/TiO_2 which identified strongly bound hydride species [38]. In addition, adsorbed CO can be seen on Pt

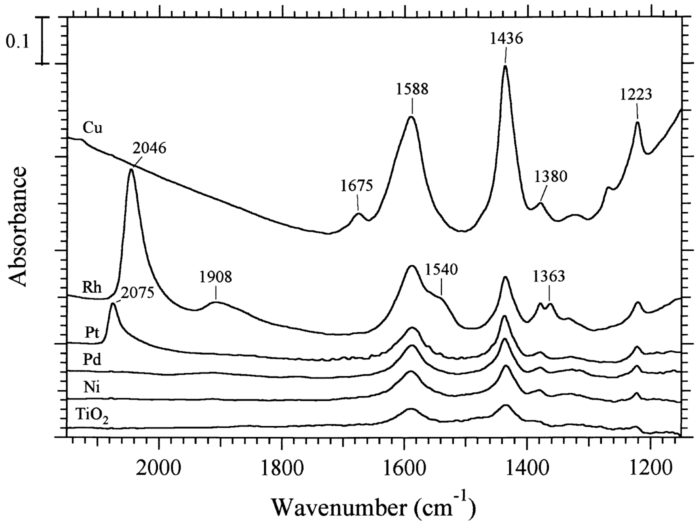

Fig. 9. DRIFT spectra during CO_2 adsorption on TiO_2 and TiO_2-supported Ni, Pd, Pt, Rn and Cu at 293 K, referenced to spectrum of the reduced catalyst prior to gas admission. Conditions: $P_{tot}\approx740$ Torr and $CO_2/Ar=1/4$.

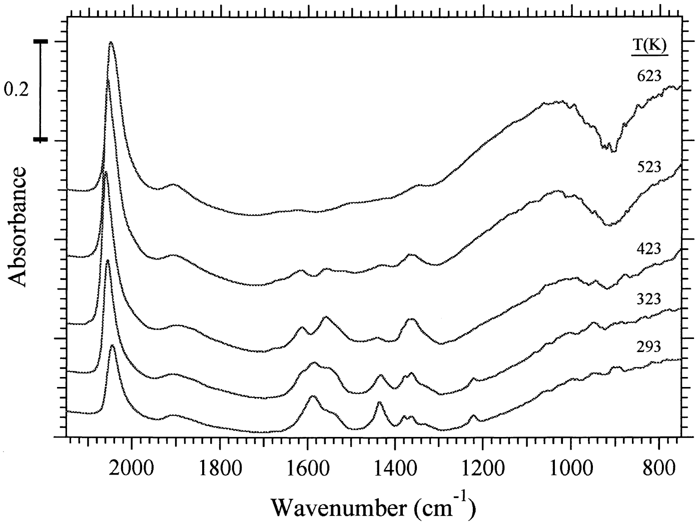

Fig. 10. DRIFT spectra during CO_2 adsorption on Rh/TiO_2 from 293 to 623 K, referenced to spectrum of the reduced catalyst prior to gas admission. Conditions: $P_{tot}\approx740$ Torr and CO_2/Ar=1/4.

(2075 cm^{-1}) and Rh (2046 and 1908 cm^{-1}), confirming the dissociation of CO_2. This is consistent with the report by Tanaka et al. [39] that TiO_x species can promote the dissociation of CO_2 on Pt at temperatures as low as 77 K . Thus, it may be proposed that Pt/TiO_2 and Rh/TiO_2 are more active than TiO_2, Cu/TiO_2, Ni/TiO_2, and Pd/TiO_2 for CO_2–CH_4 reforming because they facilitate both CH_4 (Fig. 8) and CO_2 (Fig. 9) dissociation.

DRIFT spectra of CO_2 adsorption on Rh/TiO_2 were also obtained as a function of temperature, as shown in Fig. 10. As temperature increases, the band intensities of formate, bicarbonate, and bidentate carbonate species (1700–1200 cm^{-1}) decrease, while the intensity of adsorbed CO (near 2050 cm^{-1}) increases. The loss observed above 323 K at 920 cm^{-1} indicates that surface Ti–O species participate in the activation of CO_2, as was observed during CH_4 adsorption (Fig. 8). The ready formation of chemisorbed CO at 293 K differs from the results reported by Erdöhelyi et al. [2] for Rh/SiO_2 and Rh/Al_2O_3, which showed no dissociative adsorption of CO_2 on Rh at 300 K. This can be attributed to a crystallite size effect [40]; however, TiO_x species can also facilitate CO_2 dissociation [39]. It is generally accepted that CO_2 chemisorption on a transition metal surface is dominated by electron transfer and that CO_2 dissociation requires the formation of an anionic CO_2-precursor [41,42]. In addition, the charge polarization in gas-phase CO_2 renders the carbon atom acidic [43]. Consequently, oxygen addition to the carbon atom of CO_2 could facilitate both adsorption, in the form of carbonates, and dissociation.

The aforementioned DRIFTS results indicate that surface oxygen species on silica and titania can participate in the activation of CH_4 and CO_2. However, as mentioned previously, the formation of $H_2C{=}O$ species at Ti^{+n} centers on TiO_2 and TiO_2-supported metals does not seem to depend solely on the interaction of CH_4 with surface oxygen species. Oxygen vacancies on the reduced titania surfaces have one trapped free electron and thus act as surface donors [44]; consequently, it is possible that Ti^{+n} species also participate in the dissociation of both CH_4 and CO_2. Indeed, the formaldehyde species formed on pure reduced TiO_2 (Fig. 8) supports this conclusion. These results provide additional evidence that TOFs for TiO_2-supported metals are higher than for SiO_2-supported metals because of the creation of new active sites, i.e., either metal–Ti^{+n} ($n<4$) or metal Ti^{+n}–O^{-m} sites, in the metal–support interfacial region, which can activate both CH_4 and CO_2 as well as accelerate CH_xO decomposition. These IR results are also consistent with the reaction mechanism proposed recently for CO_2 reforming of CH_4 over Ni and Pt catalysts [1,6].

4. Summary

To elucidate the role of MSI in CO_2 reforming of CH_4, the reaction was investigated over a series of SiO_2- and TiO_2-supported transition metals. Catalyst activity was found to depend on both the support and the %-d character of the metal; however, different trends were observed for metals on SiO_2 and on TiO_2. With the former, a maximum in activity was observed with Pt whereas with the latter, optimum performance was obtained with Rh. A plot of activity versus band occupancy (i.e., % d-character) reveals a similar maximum for the ammonia synthesis reaction; however, it occurs with Ru [45]. In situ DRIFT spectra after exposure to CH_4 and CO_2 revealed that oxygen from the support can react with CH_4 and CO_2 and that CH_xO species are formed during CH_4 adsorption on TiO_2-supported transition metals, presumably in the metal–titania interfacial region.

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