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CO_2 Reforming of CH_4 over Supported Ru Catalysts

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CO_2 reforming of CH_4 over Ru supported on η-Al_2O_3, TiO_2, and high-surface-area carbon black was investigated, and the catalysts were characterized using chemisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed surface reaction (TPSR). Although CO chemisorption and XRD spectra indicated high Ru dispersions (>50%), H_2 chemisorption was significantly lower. Turnover frequencies for CO_2 reforming of CH_4 were obtained in the absence of heat and mass transfer effects. These values decreased in the order Ru/TiO_2 > Ru/Al_2O_3 ≫ Ru/C, and they were found to depend strongly on the space velocity and hence the percentage of equilibrium conversion. The use of a simple power law kinetic model showed that this dependence is most likely due to a contribution from CO hydrogenation to CH_4, which constitutes part of the reverse reaction, thus emphasizing the need to work at low conversions relative to the equilibrium conversion to obtain accurate kinetic data. Correction for this contribution allowed determination of unidirectional forward rates for the CO_2/CH_4 reforming reaction on Ru. © 1999 Academic Press

Key Words: **methane; carbon dioxide; CO_2 reforming; ruthenium; titania; alumina; carbon.**

INTRODUCTION

The relative importance of natural gas as an energy resource is expected to grow significantly in the near future (1, 2). Consequently, commercial interest in the conversion of CO_2-rich natural gas into more useful products such as synthesis gas should also increase. Noble metals such as Ru are not preferable for large-scale commercial use in catalysts for CO_2 reforming of CH_4 (3); however, several studies have shown the superior activity of Ru supported on TiO_2 (4), MgO (5), and Al_2O_3 (6) in comparison to other supported group VIII metals. While Ru/Al_2O_3 catalysts have been investigated by several research groups (6–14), Ru/TiO_2 has not yet been thoroughly investigated (4, 12), and carbon-supported Ru has yet to be studied. Thus, a comparative investigation of CO_2–CH_4 reforming over Ru/Al_2O_3, Ru/TiO_2, and Ru/C was undertaken. Furthermore, equilibrium conversions for this endothermic reaction can be low; thus if experimental conversions are too near these values, the reverse reaction can alter the observed rates and complicate analysis. This consideration is also addressed in this paper.

EXPERIMENTAL

A high-surface-area commercial carbon black, Black Pearls 2000 (>1200 m^2/g, Cabot Corporation), was treated in flowing H_2 at 1230 K for 24 h to clean the surface and subsequently cooled in flowing H_2 to room temperature prior to impregnation with an aqueous solution of $RuCl_3 \cdot xH_2O$ (Alfa Products) (15). Due to the uncertainty in the hydration number of the Ru salt, the Ru loading was quantified via inductively coupled plasma spectrophotometry as 4.8 ± 0.2 wt% (16). An incipient wetness technique was used to impregnate η-Al_2O_3 (Exxon Corp., 245 m^2/g) and TiO_2 (Degussa P-25, 47 m^2/g) to prepare 1.6% Ru/Al_2O_3 and 0.5% Ru/TiO_2 catalysts, respectively. Pretreatment of the Ru catalysts prior to either reaction or chemisorption consisted of reduction in flowing H_2 at 423 K for 30 min and at 773 K for 60 min, followed by either a purge in flowing He or evacuation (10^{-7} Torr) for 30 min at 723 K to remove adsorbed hydrogen, as described previously (4, 17, 18). Because reduction of Ru/TiO_2 at 773 K is known to induce strong metal–support interaction (SMSI) behavior (19), isotherms were also obtained at 300 K after reduction of Ru/TiO_2 at 473 K to better estimate the Ru dispersion. Murata and Aika have reported that reduction in flowing H_2 near 1000 K is necessary to remove most residual Cl from supported Ru catalysts (20); consequently, *ex situ* X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Analytical XSAM800pci system using unmonochromated Mg$K\alpha$ radiation to estimate the atomic Cl/Ru ratios in the as-prepared and reduced catalysts (21). For Ru/C and Ru/Al_2O_3, the Cl/Ru ratios were calculated by integrating the intensities of the Ru 3*p* and Cl 2*p* peaks and normalizing the areas to published atomic sensitivity factors of 1.2 for Ru 3*p* and 0.77 for Cl 2*p* (21). However, the Ru 3*p* peak doublet was not detectable in the spectra for Ru/TiO_2 (21); consequently, the Cl/Ru ratios for this

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catalyst were estimated from the heights of the Ru $3d_{5/2}$ and Cl $2s$ peaks using atomic sensitivity factors of 2.15 for Ru and 0.25 for Cl (22). In addition, X-ray diffraction (XRD) was performed with a Rigaku Geigerflex sysem using filtered Cu$K\alpha$ radiation to identify the bulk phases of the reduced catalyst samples.

The temperature-programmed surface reaction (TPSR) of CO_2 with Ru/C was performed to investigate the potential for the carbon gasification reaction, i.e., $CO_2 + C \rightarrow 2\,CO$, to occur. After redution of Ru/C for 1 h at 773 K using the procedure described previously, the catalyst was purged with He for 30 min at 723 K and cooled slowly to room temperature. Subsequently, the temperature was ramped from 300 to 1000 K at the rate of 10 ± 1 K/min while a 1/1 mixture of CO_2 in He was passed over the catalyst bed at a WHSV of 45,000 $cm^3\ g^{-1}\ h^{-1}$. Concomitantly the gas phase was sampled with the on-line gas chromatograph every 2 min to monitor CO evolution and CO_2 consumption via an overall carbon balance.

A high-temperature reactor sysem, described previously (18), was used to determine catalyst activity. The amount of catalyst used during these experiments varied between 4 and 50 mg. All 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 WHSV of 24,000 to 600,000 $cm^3\ g^{-1}\ h^{-1}$ over the temperature range 673 to 723 K.

RESULTS

A summary of irreversible chemisorption values and uptake ratios as well as Cl/Ru ratios for the as-prepared and reduced catalysts is provided in Table 1. The Cl/Ru ratios obtained from these spectra are all somewhat less than the ratio of 3 present in the Ru salt precursor. More importantly, the XPS analyses illustrate that the 773 K reduction pretreatment removed some, but not all, of the Cl from the prepared catalysts. For all catalysts, H_2 adsorption is greatly suppressed relative to that of CO. Lu and Tarachuk have shown that Cl poisons up to six nearest-neighbor adsorption sites on Ru to render H_2 adsorption activated (23, 24); consequently, it is likely that suppressed H_2 adsorption is in part due to the presence of residual Cl on the Ru surface after reduction. Suppression of H_2 adsorption on Ru/C may also be due in part to interstitial carbon atoms at the surface of the Ru crystallites, as observed for Pd/C (25) and Ni/C (18). The markedly suppressed adsorption of both H_2 and CO on Ru/TiO_2 after reduction at 773 K, relative to that after reduction at 473 K, is not attributed to Ru particle sintering and indicates formation of the SMSI state with TiO_x species decorating the Ru surface, as observed previously for other TiO_2-supported metals (4, 17, 18). The high CO/H ratios for all catalysts obtained from irreversible chemisorption measurements, which range from 4 to 35, are consistent with Ru particle sizes on the order of 1 to 2 nm (24). The CO/Ru ratios are above unity for Ru/TiO_2 and Ru/C and indicate the possibility of carbonyl formation, which is a reaction that occurs with very small Ru particles and thus also implies high dispersion. For CO/Ru ratios greater than one, a dispersion of unity was assumed.

XRD spectra of the three supported Ru catalysts after reduction at 773 K are shown in Fig. 1. The XRD spectrum of Ru/C reveals only sharp reflections due to the Al sample holder and weak, broad peaks attributed to the carbon support. The XRD spectrum of Ru/Al_2O_3 reveals only reflections due to η-Al_2O_3, while the XRD spectrum of Ru/TiO_2 reveals sharp reflections due to both anatase and rutile as well as weak reflections due to the Al sample holder. The absence of reflections due to Ru in all spectra indicates that the Ru crystallites are very small, i.e., <3 nm, in agreement with conclusions derived from H_2 and CO chemisorption.

The TPSR spectrum obtained during the interaction of CO_2 with Ru/C is shown in Fig. 2. A maximum in CO formation occurs at 990 K; however, the rate of CO formation during TPSR is negligible below 723 K and orders of magnitude lower than that observed during CO_2–CH_4 reforming (see Table 2). Therefore, although CO_2 can both dissociate and interact with carbon on the Ru/C catalysts to yield CO at high enough temperatures, these interactions can be neglected during CO_2–CH_4 reforming experiments provided that the reaction temperature is maintained below 723 K.

The turnover frequencies for the net rate of CO formation, TOF_{CO} (s^{-1}), during CO_2–CH_4 reforming at 723 K,

TABLE 1

Chemisorption Uptakes and Cl/Ru Ratios for Supported Ru Catalysts

Catalyst	T_{red} (K)	U_{irr} (μmol/g_{cat})		H_{ad}/Ru_{total}	CO_{ad}/Ru_{total}	Cl/Ru ratio[a]	
		H_2	CO			As prepared	Reduced
4.8% Ru/C	773	20.2	587	0.085	1.2	2.2	0.3
1.6% Ru/Al_2O_3	773	14.7	123	0.19	0.78	2.5	1.6
0.5% Ru/TiO_2	773	1.3	26.6	0.051	0.51	2.8	1.9
	473	3.0	107	0.11	3.9	—	—

[a] From XPS.

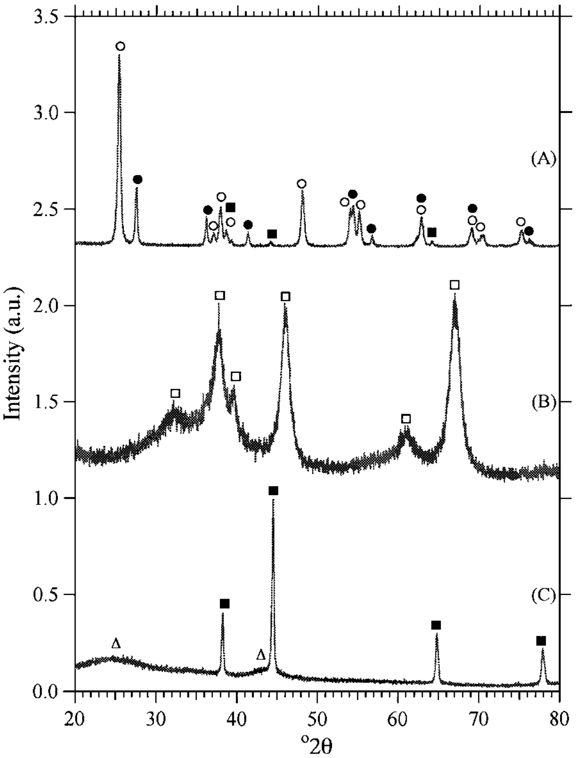

FIG. 1. XRD spectra of (A) Ru/TiO_2, (B) Ru/Al_2O_3, and (C) Ru/C after reduction at 773 K: (○) Anatase, (●) rutile, (☐) η-Al_2O_3, (■) Al sample holder, (Δ) carbon.

TABLE 2

Comparison of Turnover Frequencies on Supported Ru Catalysts at 723 K

	$TOF_{CO} = TOF_{for} - k_r P_{H_2}^{\gamma} P_{CO}^{\delta}$					
Catalyst	γ^a	δ^a	k_r ($Torr^{-(\gamma+\delta)}$ s^{-1})	TOF_{for} (s^{-1})	$TOF_{CO}{}^b$ (s^{-1})	Ψ^c
Ru/TiO_2	2.0 ± 0.2	-0.5 ± 0.2	0.026	9.1	7.4	0.07
Ru/Al_2O_3	1.6	−0.6	0.087	3.5	2.9	0.14
Ru/C	1.8^d	-0.55^d	0.002	0.24	0.2	0.04

[a] Values obtained from Ref. (28).

[b] Maximum TOF observed at highest experimental WHSV (see Fig. 3).

[c] Weisz criterion (26).

[d] A mean of the values used for Ru/TiO_2 and Ru/Al_2O_3.

calculated by normalizing the activity ($\mu mol/s \cdot g_{cat}$) to the Ru dispersion determined by irreversible CO adsorption after reduction at 773 K, were found to be very dependent on the space velocity for all three supported Ru catalysts, as shown in Fig. 3. Turnover frequencies for CH_4 consumption (not shown for brevity) follow the same trend and clearly indicate that it is not an artifact due to the reverse water–gas shift (RWGS) reaction. The TOF_{CO} values obtained at the highest space velocity are listed in Table 2. Weisz criterion (Ψ) calculations confirm the absence of diffusional effects, i.e., for all cases $\Psi < 0.3$ (26), as indicated in Table 2,

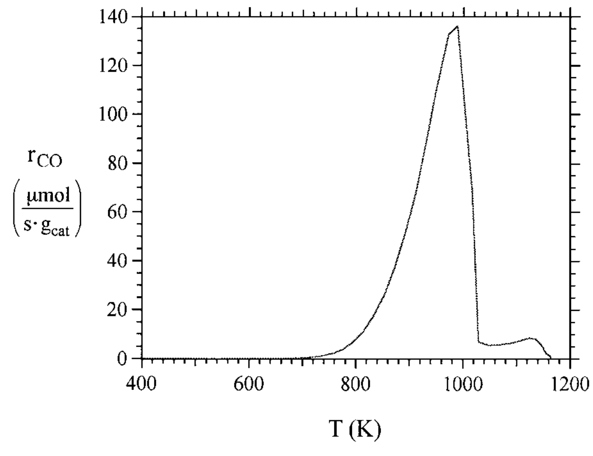

FIG. 2. TPSR spectrum for the interaction of CO_2 with reduced Ru/C. Conditions: $CO_2/He = 1/1$, $P = 1$ atm, WHSV = 45,000 cm^3 g^{-1} h^{-1}, $\beta = 10 \pm 1$ K/min.

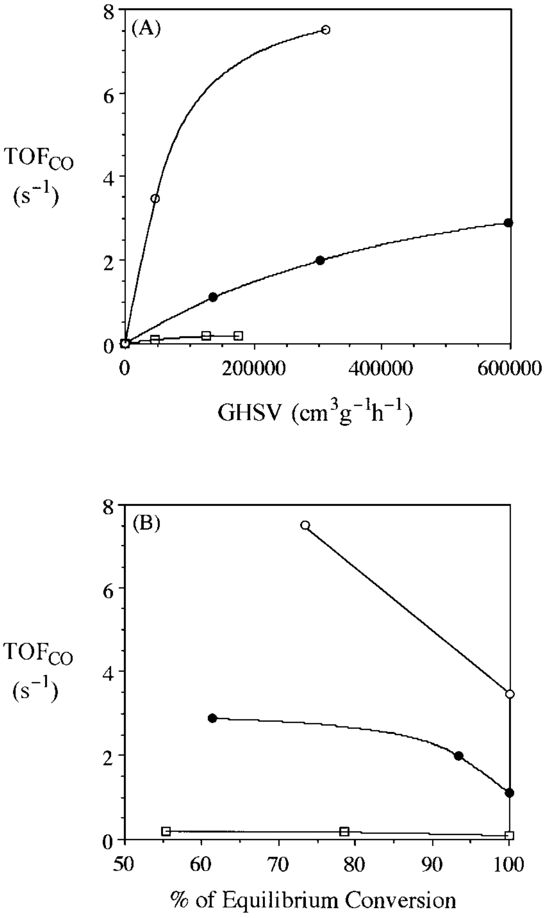

FIG. 3. Observed (i.e., net) TOF for CO formation at 723 K as a function of (A) WHSV and (B) percentage equilibrium conversion for (○) Ru/TiO_2, (●) Ru/Al_2O_3, and (☐) Ru/C. Reaction conditions: $CH_4/CO_2/He = 1/1/1.8$, $P = 1$ atm.

and the use of these very high space velocities would also minimize or eliminate any external mass transfer effects. In addition, use of the criterion discussed by Anderson (27) to determine the absence of heat transfer limitations, i.e., $|-\Delta H|\mathcal{R}r^2/\lambda T_s < 0.75\ RT_s/E$, where ΔH is the heat of reaction, $\mathcal{R}$ is the reaction rate, r is the particle radius, λ is the catalyst thermal conductivity, T_s is the reaction temperature, R is the gas constant, and E is the apparent activation energy, showed that the value of the left-hand term was consistently 10^{-2}–10^{-3} that of the right-hand term; thus no heat transfer effects were present. All results indicate that the percentage equilibrium conversion, i.e., the degree of influence of the reverse reaction, is the important variable. Supported Ru catalysts are very active for CO hydrogenation to CH_4 (28); accordingly, an empirical analysis of the kinetic data in Fig. 3 indicates that the observed trend in TOF with space velocity is likely caused by a decrease in the effect of the reverse reaction, i.e., CO hydrogenation to CH_4, due to the lower conversions at higher space velocities. This reaction coupled with the water–gas shift reaction, which is quasi-equilibrated under these conditions (29, 33), constitutes the overall reverse reaction. If the observed TOF for the net rate of CO_2–CH_4 reforming at 723 K, TOF_{obs}, is influenced by the reverse reaction, then the net rate can be approximated by the expression

$$TOF_{obs} = TOF_{for} - TOF_{rev}, \qquad [1]$$

where TOF_{for} is the turnover frequency for the forward CO_2–CH_4 reforming reaction (including the reverse water–gas shift reaction) and TOF_{rev} is the turnover frequency for the reverse, rate-determining methanation reaction. If a general power rate law is assumed for CO hydrogenation to CH_4,

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

then a plot of TOF_{obs} values at each WHSV versus $P_{H_2}^{\gamma} P_{CO}^{\delta}$ should be linear, with the slope being equal to $-k_r$ at 723 K.

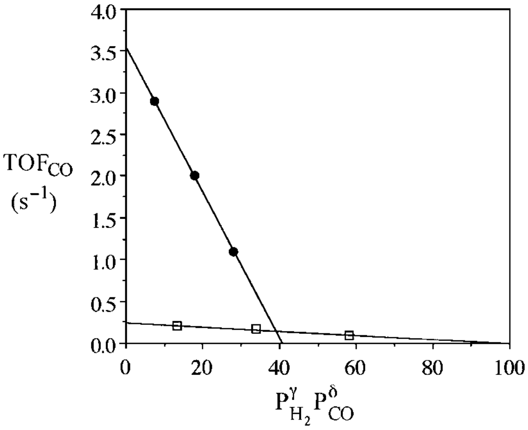

FIG. 4. Observed (i.e., net) TOF for CO formation at 723 K over (●) Ru/Al_2O_3 and (☐) Ru/C as a function of the effluent partial pressures of H_2 and CO. See text and Table 2 for details. Reaction conditions: $CH_4/CO_2/He = 1/1/1.8$, $P = 1$ atm.

Plots of TOF_{obs} versus $P_{H_2}^{\gamma} P_{CO}^{\delta}$ were constructed for both TOF_{CO} and TOF_{CH_4} values for each catalyst and were found to be linear, as shown for Ru/Al_2O_3 and Ru/C in Fig. 4. Values of TOF_{for} and k_r obtained from these analyses are provided in Table 2. The calculated values of the "true" forward TOFs for CO_2–CH_4 reforming at 723 K, TOF_{for}, are in close proximity to the maximum TOFs observed experimentally at the highest space velocities, TOF_{max}, indicating that at sufficiently high space velocities and low enough conversions the kinetic data were not significantly influenced by the reverse reaction. The calculated value of k_r for Ru/C at 723 K is much lower than that for either Ru/TiO_2 or Ru/Al_2O_3, in agreement with the general observation that carbon-supported Ru is much less active for CO hydrogenation to CH_4 than Ru supported by metal oxides (29). Thus, this empirical rate analysis indicates that sufficiently high space velocities must be used to maintain low conversions and thus minimize the influence of the reverse reaction during kinetic studies of CO_2–CH_4 reforming. The use of high WHSVs results in lower CH_4 and CO_2 conversions which decrease the effluent partial pressures of H_2 and CO and thereby minimize the influence of both the RWGS reaction and the reverse reaction. Consequently, not only the observed TOF for CO_2–CH_4 reforming but also the apparent energy can be influenced for the space velocity if it becomes too low, as shown in Fig. 5 for Ru/Al_2O_3.

Initial net catalyst activities and turnover frequencies at 723 K as well as apparent activation energies, E_{app}, obtained

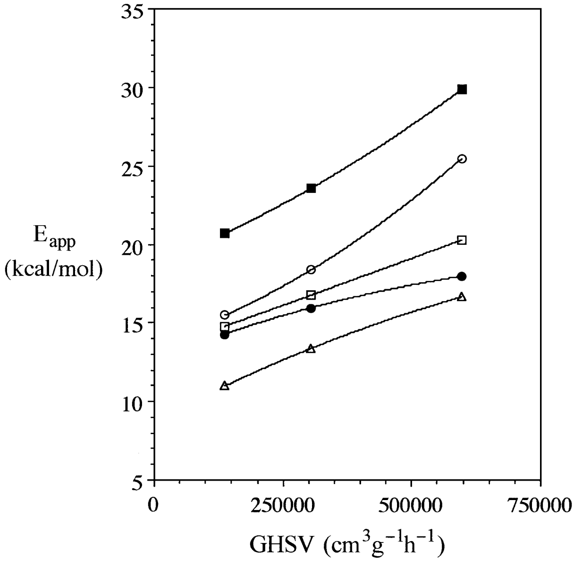

FIG. 5. Variation of apparent activation energies, E_{app}, with WHSV for (○) CH_4 and (●) CO_2 consumption as well as for the formation of (☐) CO, (■) H_2, and (Δ) H_2O during CH_4–CO_2 reforming over Ru/Al_2O_3. Reaction conditions: $CH_4/CO_2/He = 1/1/1.8$, $P = 1$ atm.

TABLE 3

Linear Deactivation Rate, Catalyst Activity at 723 K, and Apparent Activation Energy for Supported Ru Catalysts

Catalyst	Deactivation (%/h)	Conversion (%)		Activity[a]			E_{app} (kcal/mol)				
		CH_4	CO_2	Specific (μmol CO/s $\cdot$ g_{cat})	TOF_{CO}[b] (s^{-1})	TOF_{CH_4}[b] (s^{-1})	CH_4	CO_2	CO	H_2	H_2O
Ru/TiO_2	1.4 ± 1.1	7.4	12.2	197	7.4 4.0[c]	2.8 1.5[c]	18.2	17.1	17.5	23.2	14.6
Ru/Al_2O_3	0.3	6.2	12.3	357	2.9	0.97	25.5	18.0	20.3	29.9	16.7
Ru/C	5.1	5.6	11.1	97	0.20[c]	0.07[c]	25.7	20.6	22.2	26.2	20.8

[a] Highest net activity at 723 K during initial 30 min on stream.

[b] Based on irreversible CO adsorption after reduction at 773 K.

[c] Assuming 100% Ru dispersion.

at high WHSVs are compared in Table 3. On a TOF basis, the order of catalyst activity for CO_2–CH_4 reforming is $Ru/TiO_2 > Ru/Al_2O_3 \gg Ru/C$, and the same trend exists for the forward, unidirectional TOF_{CO} values in Table 2. Observed CO_2 conversions were always greater than those of CH_4. In addition, apparent activation energies for H_2 formation are higher than those for CO and H_2O, indicating the influence of the RWGS reaction as discussed in detail elsewhere (17, 18). Consequently, measured H_2/CO ratios were always less than unity. Note that in the absence of carbon deposition and C_2^+ formation, reaction stoichiometry demands that

$$\frac{H_2}{CO} = \left(3 - r_{CO_2}/r_{CH_4}\right)/\left(1 + r_{CO_2}/r_{CH_4}\right), \qquad [3]$$

where r_{CH_4} and r_{CO_2} are the experimental rates of CH_4 and CO_2 conversion, respectively.

DISCUSSION

The highest TOF for CH_4 consumption obtained in this study at 723 K over Ru/Al_2O_3 is compared in Table 4 with TOFs based on the studies by Solymosi *et al.* (10), Basini and Sanfilippo (12), Mark and Maier (14), and Claridge *et al.* (6). Direct comparison is difficult due to the wide range of reaction conditions used; however, an effort has been made here to do so by correcting all reported TOFs to the same experimental conditions, i.e., $P_{CH_4} = P_{CO_2} = 200$ Torr and $T = 723$ K, using the following power rate law expression:

$$TOF_{CH_4} = A \exp\left(-E_{CH_4}/RT\right) P_{CH_4}^{\bar{\alpha}} P_{CO_2}^{\bar{\beta}}. \qquad [4]$$

Values of the apparent activation energy, E_{CH_4}, reported by Solymosi *et al.* (10) and Claridge *et al.* (6) were preferentially used with their own data for self-consistency. Basini and Sanfilippo (12) and Mark and Maier (14) did not report E_{CH_4} values; thus, a mean value ($\pm 1\sigma_n$) of 20.2 ± 5.3 kcal/mol was used to extrapolate their TOF data. Mean values of $\bar{\alpha}$, 0.52 ± 0.36, and $\bar{\beta}$, 0.21 ± 0.40, were calculated based on all α and β values reported in the literature for CH_4 (30). It is of interest that these approximate "standard" TOFs at 723 K still correlate with the space velocity, in agreement with Fig. 3, suggesting that the relatively low TOF values may be due to the effect of the overall reverse reaction, of which CO hydrogenation to CH_4 consitutes the initial reaction. This conclusion is supported by data in the original references. For example, the TOF reported by Basini and Sanfilippo was measured at an extremely low space velocity near equilibrium conversion (12). The initial CH_4 conversion of 7.5% at 823 K measured by Solymosi *et al.* (10)

TABLE 4

TOFs for CO_2–CH_4 Reforming over Ru/Al_2O_3 Compared under Identical Conditions

Catalyst	Precursor	H/Ru	Experimental data					Standard TOF_{CH_4}[a] (s^{-1})	Reference
			GHSV (h^{-1})	P_{CH_4} (Torr)	T (K)	E_{CH_4} (kcal/mol)	TOF_{CH_4} (s^{-1})		
1.6% Ru/η-Al_2O_3	$RuCl_3 \cdot H_2O$	0.19	595,500	200	723	25.5	0.97	0.97	This study
5% Ru/Al_2O_3	—	0.016	440,000	380	723	13	0.62	0.40	(6)
0.5% Ru/γ-Al_2O_3	$RuCl_3 \cdot H_2O$	0.35	30,000	380	973	—	2.00	0.03	(14)
1% Ru/Al_2O_3	$RuCl_3 \cdot H_2O$	0.055	6,000	380	823	22.1	0.53	0.05	(10)
Ru/α-Al_2O_3	$Ru_3(CO)_{12}$	0.95	3,000	570	1023	—	1.05	0.008	(12)

[a] Extrapolated to "standard" conditions, i.e., $P_{CH_4} = P_{CO_2} = 200$ Torr and $T = 723$ K, using $TOF_{CH_4} = A\ \exp(-E_{CH_4}/RT) P_{CH_4}^{\bar{\alpha}} P_{CO_2}^{\bar{\beta}}$. See Discussion for details.

is about one-third that expected at thermodynamic equilibrium under their reaction conditions. Consequently, the use of low space velocity, and thus large residence time, can result in the strong influence of the reverse reaction.

XPS analysis of the as-prepared and reduced $Ru/\eta\text{-}Al_2O_3$ catalysts in this investigation supported the proposal that the discrepancy between irreversible H_2 and CO uptakes prior to use in the reaction is due in part to coverage of the Ru surface by Cl originating from the $RuCl_3$ precursor, as discussed previously. Thus, the low Ru dispersions for Ru/Al_2O_3 based on H_2 chemisorption, as reported by Solymosi *et al.* (10), Mark and Maier (14), and Claridge *et al.* (6), may also reflect partial coverage of the Ru surface by Cl. Basini and Sanfilippo (12), however, prepared their Ru/Al_2O_3 catalyst with $Ru_3(CO)_{12}$, rather than a Cl salt precursor. The relatively high dispersion that they measured by H_2 adsorption, ∼0.95, is consistent with our CO chemisorption (Table 1) and XRD results (Fig. 1), indicating that Ru can be well dispersed on an Al_2O_3 surface. Further evaluation to quantify the Ru dispersion, e.g., by HRTEM, was beyond the scope of this investigation. It is not possible to determine from the data obtained here whether or not the interaction of Cl with the Ru surface, during which Cl may geometrically block adsorption sites as well as induce a nearest-neighbor ligand effect, significantly affects the kinetics of CO_2–CH_4 reforming. Gudde and Lambert have shown that the adsorption of Cl on Ru(100) increases the work function, and hence the ionization potential (IP), of the Ru surface (31). Also, Trevor *et al.* have shown that the reactivity of CH_4 with Pt clusters in the gas phase increases as the IP of the cluster increases (32). Thus, it seems possible that Cl could promote CO_2–CH_4 reforming over supported Ru by facilitating CH_4 activation. Indeed, the relative catalyst activities measured in this investigation (Table 3) correlate with measured initial Cl/Ru ratios on the reduced catalysts (Table 1). However, the presence of steam under reaction conditions could facilitate Cl removal and minimize its influence on kinetic behavior. Additional studies are necessary before any nonspeculative conclusion can be made.

Based on turnover frequencies, the order of catalyst activity for CO_2–CH_4 reforming obtained in this investigation is $Ru/TiO_2 > Ru/Al_2O_3 \gg Ru/C$, as shown in Fig. 3 and Tables 2 and 3. The irreversible CO uptake on Ru/TiO_2 after reduction at 773 K was significantly suppressed relative to that measured after reduction at 473 K, as shown in Table 1. *In situ* diffuse reflectance Fourier transform infrared (DRIFT) spectra of this catalyst during reduction at 773 K clearly demonstrated Ti–O bond cleavage and indicated TiO_x formation (4, 30); thus, metal–support interactions are created in this catalyst. Via controlled deposition of TiO_x onto Pt powder, it has been demonstrated that TiO_x species on a metal surface greatly promote catalyst activity for CO_2–CH_4 reforming, presumably because of the creation of a large number of interfacial sites (33). Under these reaction conditions, kinetic data have been fit well by a rate expression derived from a sequence of steps invoking a slow, reversible, dissociative CH_4 adsorption step to form $CH_{x,\mathrm{ad}}$ species as well as a slow, irreversible step for the decomposition of a surface CH_xO species to form CO and hydrogen (17, 30, 34). The reverse water–gas shift reaction is quasi-equilibrated. Details and assumptions related to this model have been discussed in detail in these previous papers. Thus, the superior activity of Ru/TiO_2 in comparison to Ru/Al_2O_3 and Ru/C may be due to the presence of interfacial $Ru\text{–}Ti^{n+}O_x$ sites which can markedly enhance the rates of these two processes.

The activity of the Ru/C catalyst on a TOF basis is an order of magnitude lower than that of either Ru/TiO_2 or Ru/Al_2O_3, as shown in Table 3. In contrast to the latter two catalysts, reduced carbon-supported Ru should have no interfacial cation sites; thus, in the context of the previous paragraph, Ru/C might be expected to be the least active for CO_2–CH_4 reforming. Although CH_4 dissociation on Ni surfaces (35) and CO_2 reduction on Pt surfaces (36) are structure sensitive, the rates of formation of C_2 and C_3 hydrocarbons from CH_4 over $Ru(11\bar{2}0)$ are only about two times higher than for Ru(0001) (37); thus, the relatively low activity of Ru/C is not likely to be due to severe structure sensitivity. Nevertheless, in the absence of microscopic information that clearly defines the structure of the Ru crystallites in these catalysts, the relative importance of Ru structure to catalyst activity for CO_2–CH_4 reforming cannot be evaluated at this time.

SUMMARY

Evidence is presented that illustrates that the specific activity and apparent activation energy of supported Ru catalysts for CO_2–CH_4 reforming can be quite dependent on the space velocity because it can control the percentage equilibrium conversion and thus the influence of the reverse reactions: slow CO hydrogenation to CH_4 followed by the quasi-equilibrated water–gas shift reaction. With this perspective, it is possible to reconcile significant differences in TOFs reported in the literature for Ru/Al_2O_3 catalysts. On a TOF basis, the order of catalyst activity is found to decrease in the order $Ru/TiO_2 > Ru/Al_2O_3 \gg Ru/C$ under conditions where heat and mass transfer limitations do not exist. The same trend exists for both the net TOF and the unidirectional forward TOF values, and the TOF on Ru/TiO_2 is 40-fold higher than that on Ru/C.

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