

Spillover of CO and H₂ onto Al₂O₃ SurfacesBISHWAJIT SEN, JOHN L. FALCONER,¹ TIAN-FU MAO, MIN YU,
AND RAYMOND L. FLESNER*Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424*

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Temperature-programmed reaction and desorption (TPR, TPD) for Al₂O₃ physically mixed with supported Ni catalysts show directly that one of the two CH₄ peaks observed previously for TPR (CO hydrogenation) on Ni/Al₂O₃ catalysts results from spillover of adsorbed species onto Al₂O₃ and is not due to adsorption on unreduced Ni sites. Temperature-programmed desorption from physical mixtures of Al₂O₃ and 19% Ni/Al₂O₃ indicates that the support-bound species is a H-CO complex, and the stoichiometry is consistent with that of a CH₃O species. The concentration of CH₃O on Al₂O₃ is estimated to be approximately 1 μmol/m² Al₂O₃ (350 μmol/g Al₂O₃). Though CH₃O does not form on the SiO₂ support of Ni/SiO₂, it does form on physical mixtures of Ni/SiO₂ and Al₂O₃ that were prepared to provide good contact between particles. The rate of spillover appears to increase with the closer proximity between the support and the catalyst, higher Ni surface area, and better contact between the particles, but it also depends on the Al₂O₃ area available for transfer. The rate of CH₃O hydrogenation increases with Ni surface area. An unexplained loss in Ni surface area was observed with physical mixtures of Al₂O₃ and catalysts that were prepared by crushing the particles while wet. © 1990 Academic Press, Inc.

INTRODUCTION

Several studies have reported that two distinct types of methanation sites are present on Al₂O₃-supported catalysts (Ni, Co, Ru, and Pt) (1-5). These two types of sites resulted in two distinct CH₄ peaks when adsorbed CO was hydrogenated during temperature-programmed reaction (TPR). Kester and Falconer (1) first attributed these two peaks on Ni/Al₂O₃ to CO adsorbed on Ni particles and CO adsorbed on Ni atoms that were interacting with an oxide phase. These two types of adsorbed CO reacted at different rates to form CH₄. Based on XPS observations, Huang *et al.* (6) attributed the two CH₄ peaks on Ni/Al₂O₃ catalysts to CO adsorbed on Ni and CO adsorbed on a surface aluminate, which formed during catalyst preparation and was not reduced to metallic Ni at 775 K. More recent studies on Ni/Al₂O₃ (7-9) and Ru/Al₂O₃ (4), however, concluded that one of the CH₄ peaks was

due to hydrogenation of CO adsorbed on Ni metal and the other was due to hydrogenation of a H-CO complex that was adsorbed on the Al₂O₃ support. The stoichiometry of the complex, as identified by temperature-programmed desorption (TPD) of coadsorbed CO and H₂, was that of a CH₃O species. Direct identification of a CH₃O species on Pt/Al₂O₃ was made by IR spectroscopy, and the combination of IR and TPR on Pt/Al₂O₃ showed that the CH₃O was hydrogenated at a different rate than was CO adsorbed on Pt (5). As a result, two CH₄ peaks were detected during TPR for CO adsorbed on Pt/Al₂O₃, and the CH₃O was concluded to be present on the Al₂O₃ surface.

The H-CO complex on Ni/Al₂O₃ catalysts is formed by the interaction of H and CO, which were adsorbed on the metal surface and then spilled over onto the Al₂O₃ (7), where the complex was stable. Isotope labeling was used to show directly that transfer occurred between the adsorption sites on the surface (7). The complex was concluded to be adsorbed on the Al₂O₃ sup-

¹ To whom correspondence should be addressed.

port because: (a) the total amount of adsorbed CO on Ru/Al₂O₃ (4) was three times larger than the total number of Ru atoms present in the catalyst, (b) the saturation surface concentrations of the complex (normalized per g-Al₂O₃) were similar for 5.1% Ni/Al₂O₃, 19% Ni/Al₂O₃, and 1% Ru/Al₂O₃ (4, 7, 9), and (c) CH₃O was not stable above room temperature on Ni surfaces.

In the present experiments we have attempted to determine directly the location of the H-CO complex on a Ni/Al₂O₃ catalyst and to characterize the spillover process. If the CO transfers to the Al₂O₃ by a spillover process, then more CO should spillover if additional Al₂O₃ is placed in physical contact with a supported Ni catalyst (10). Thus, TPR and TPD experiments were carried out on physical mixtures comprising equal amounts of Al₂O₃ and a reduced and passivated, supported Ni catalyst. A 19% Ni/Al₂O₃ catalyst and a 9.5% Ni/SiO₂ catalyst were used as the two sources of Ni. A high weight loading Ni/Al₂O₃ catalyst was used because the high Ni surface area creates a large source for spillover, which thus should be faster than the spillover for a low loading catalyst (2). Also, the high loading Ni/Al₂O₃ catalyst is almost completely reduced, and thus the role of a nickel aluminate is minimized. Only one methanation site exists on Ni/SiO₂ catalysts (9, 11). Consequently, mixtures of 9.5% Ni/SiO₂ and Al₂O₃ were used to determine if Ni/SiO₂ can act as a source for this spillover process and to examine if the Al₂O₃ could provide sites for stabilization of the H-CO complex.

The mixtures were prepared by crushing the components together to obtain close proximity between the Al₂O₃ and the catalyst. Some mixtures were crushed while dry, and others were crushed while wet in an effort to improve the contact between the particles. Some TPR and TPD experiments were also carried out for a bed of 9.5% Ni/SiO₂ catalyst resting on a bed of Al₂O₃. The arrangement was used in the downflow reactor to determine if long-range gas-phase

transport of the spillover species occurs from the Ni crystallites to the Al₂O₃ support.

Results presented here show directly that the complex or its precursor forms on the reduced Ni phase and spills over to the Al₂O₃ support. The H-CO complex on Al₂O₃ is hydrogenated at a slower rate than is CO on Ni. We have also shown that a H-CO complex or its precursor forms on a Ni/SiO₂ catalyst, but Al₂O₃ is necessary to stabilize the complex. The rate of spillover depends on the contact between particles, the Ni surface area, the available Al₂O₃ surface area, and the proximity of Ni to Al₂O₃.

EXPERIMENTAL METHODS

The experimental system is similar to that described previously (12). A 100-mg sample of catalyst (or catalyst mixture) in a downflow tubular reactor was heated by an electric furnace at 1 K/s. The flowing gas was either He (100 cm³/min (STP)) for TPD experiments or H₂ (100 cm³/min (STP)) for TPR experiments at ambient pressure. A small thermocouple, whose tip was in the catalyst sample, measured the catalyst temperature. Effluent from the reactor was analyzed immediately downstream with a quadrupole mass spectrometer. A computer system recorded the catalyst temperature and allowed multiple mass peaks to be detected simultaneously by the mass spectrometer.

Three types of Al₂O₃-catalyst mixtures were used in these studies:

(1) 50 : 50 physical mixtures of Al₂O₃ and Ni catalysts that are referred to as wet mixtures. The Al₂O₃ and the Ni catalysts were crushed separately and mixed together. Water was then added to the mixture until excess water, beyond that required to fill the pores, was present and the wet mixture was crushed with a mortar and pestle. The Al₂O₃-Ni/SiO₂ mixtures were crushed for 10 min. Some of the Al₂O₃-Ni/Al₂O₃ mixtures were crushed up to 30 min. The crushed mixture was then dried in a vacuum oven at 375 K for 24 h and crushed again. The water was used in this procedure in

an attempt to increase contact between the particles. Several mixtures were prepared by this procedure for each of the Ni catalysts.

(2) 50 : 50 physical mixtures of Al₂O₃ and Ni catalysts that are referred to as dry mixtures. The Al₂O₃ and the Ni catalyst were crushed separately, mixed together dry, and crushed again for 10 min with a mortar and pestle.

(3) A bed of 9.5% Ni/SiO₂ (50 mg) on top of a bed of Al₂O₃ (50 mg).

Reduced and passivated Ni/SiO₂ and Ni/Al₂O₃ catalysts were used to prepare these mixtures, and the same Al₂O₃ (Kaiser A-201) that was used to prepare the Ni/Al₂O₃ catalyst was used in the mixtures. The catalysts were prepared by impregnation of nickel nitrate to incipient wetness, drying in vacuum, and direct reduction in H₂ (2). The weight loading of the catalysts were determined by atomic absorption. The Al₂O₃ surface area was 315 m²/g (9). The TPR and TPD results for the Ni/SiO₂ and the Ni/Al₂O₃ catalysts were reported previously (9). We also carried out TPR experiments on a 19% Ni/Al₂O₃ catalyst sample that had been crushed while wet, using the same procedure as used for the mixtures.

Temperature-programmed reaction (TPR) was carried out by adsorbing CO at 300 or 385 K in H₂ flow or at 300 K in He flow. A pneumatic pulse valve was used to inject a CO pulse into the carrier gas every 30 s. This procedure minimizes total CO exposure and thus minimizes the formation of nickel carbonyl at 385 K. Exposure times up to 30 min at 300 K and up to 120 min at 385 K were used. All the injected CO did not adsorb at 385 K and thus much of it was flushed out of the reactor. After adsorption was complete, the catalyst (or catalyst mixture) was heated in H₂ from 300 to 775 K while CH₄, CO, and CO₂ signals were monitored. The CH₄ signal was monitored by mass 15. The CO₂ signal amplitude was below the spectrometer detection limit. Before the initial TPR experiment, the catalyst (or catalyst mixture) was heated in H₂ for 2 h at 775 K. Before each

subsequent TPR, the catalyst was held in H₂ at 775 K for 15–30 min. For CO adsorption in He, the catalyst was cooled from 775 to 300 K in He flow. For CO adsorption in H₂, the catalyst was cooled in H₂ from 775 K. Though all TPR experiments were carried out by raising the temperature from 300 to 775 K, some of the CH₄ spectra presented in the figures only show the temperature range where CH₄ formed.

For TPD of coadsorbed CO and H₂, the catalyst (or catalyst mixture) was held in H₂ for 15–30 min at 775 K before cooling to 300 or 385 K and carrying out CO adsorption in H₂ flow. Flow was switched to He at 300 K and the catalyst (or catalyst mixture) was held at 300 K for 20–30 min before heating in He to obtain a TPD. The mass signals for H₂ (2), CO (28), CO₂ (44), and CH₄ (15) were monitored during TPD. No CH₄ was detected during TPD for the Al₂O₃–Ni/SiO₂ physical mixtures, nor for the Ni/SiO₂ catalyst resting on a bed of Al₂O₃. The mass 28 signal was corrected for CO₂ cracking.

RESULTS

Temperature-Programmed Reaction

Most of the CO that adsorbs on Ni/Al₂O₃ and Ni/SiO₂ catalysts is hydrogenated to CH₄ during a TPR experiment and thus only the CH₄ spectra are presented here. For CO adsorption at 300 K in He flow on the 19% Ni/Al₂O₃ catalyst alone, two overlapping CH₄ peaks were observed (1020 μmol CH₄/g Ni), and the peak maximas were at 465 and 484 K, as shown in Fig. 1a (2, 9). For adsorption in H₂, more CO adsorbed and the two peaks were less clearly seen (2). Isotope labeling (¹²CO and ¹³CO adsorbates) showed clearly that two distinct CH₄ peaks are present on this catalyst (9). Much more CO adsorbed at 385 K in H₂ flow than at 300 K, and the additional CH₄ was in the high-temperature peak, as shown in Fig. 2a for 30 min exposure to CO. The surface appeared to be saturated at longer times, and Fig. 3a shows the CH₄ spectrum obtained after 120 min of CO exposure. The CH₄ peak

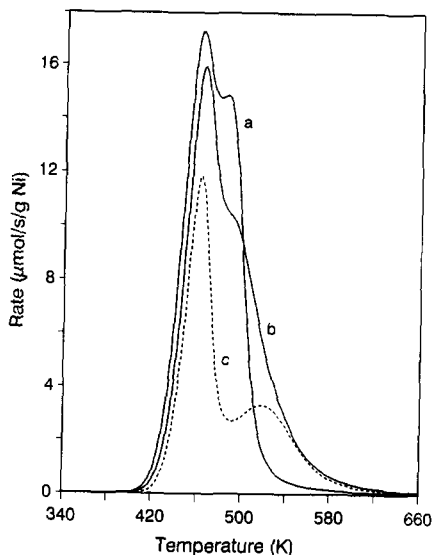


FIG. 1. Methane spectra from TPR of CO adsorbed in He flow for 30 min at 300 K on: (a) 19% Ni/Al₂O₃, (b) a 50:50 physical mixture (dry) of Al₂O₃ and 19% Ni/Al₂O₃, (c) a 50:50 physical mixture (wet) of Al₂O₃ and 19% Ni/Al₂O₃.

maximum was at 508 K, and 2530 μmol of CH₄/g Ni were formed. Note the difference in rate scales for Figs. 1–3.

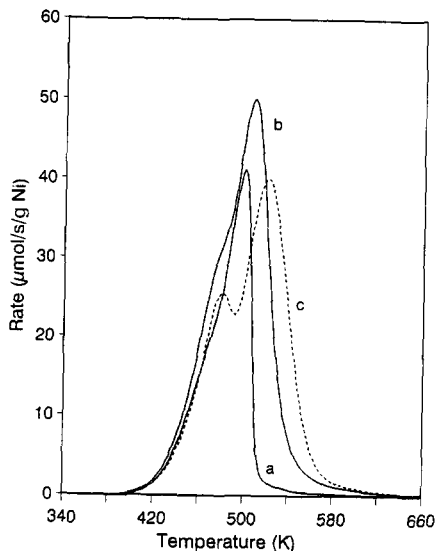


FIG. 2. Methane spectra from TPR of CO adsorbed in H₂ flow for 30 min at 385 K on: (a) 19% Ni/Al₂O₃, (b) a 50:50 physical mixture (dry) of Al₂O₃ and 19% Ni/Al₂O₃, (c) a 50:50 physical mixture (wet) of Al₂O₃ and 19% Ni/Al₂O₃.

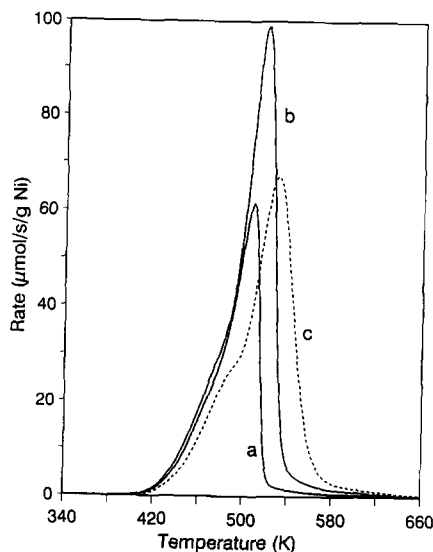


FIG. 3. Methane spectra from TPR of CO adsorbed in H₂ flow for 120 min at 385 K on: (a) 19% Ni/Al₂O₃, (b) a 50:50 physical mixture (dry) of Al₂O₃ and 19% Ni/Al₂O₃, (c) a 50:50 physical mixture (wet) of Al₂O₃ and 19% Ni/Al₂O₃.

Similar TPR results were obtained when the 19% Ni/Al₂O₃ catalyst was crushed for 2 min while wet before it was dried and placed in the TPR apparatus. The amount of CH₄ formed following CO adsorption at 300 K was 20% smaller, but the peak shapes and the location of the peak maximum were the same. The high-temperature peak showed a slight preferential decrease in amplitude. When CO was adsorbed at 385 K for 120 min, the TPR spectrum was almost identical to that in Fig. 3a.

For the 50:50 Al₂O₃–Ni/Al₂O₃ physical mixture (dry), the TPR spectrum following adsorption at 300 K (Fig. 1b) is similar to that in Fig. 1a. The amount of CH₄ formed was essentially the same for the dry mixture as for the catalyst alone, *when normalized per gram of Ni*, but the high-temperature CH₄ peak was significantly broader for the mixture. The amount of CH₄ formed following CO adsorption for 30 min at 385 K (3000 μmol CH₄/g Ni), however, was significantly larger than that observed for 120 min exposure of CO at 385 K for the catalyst alone. As shown in Fig. 2b, the curve shape was

TABLE 1
Methane Amounts During Temperature-Programmed Reaction

Catalyst	CH ₄ Amount (μmol/g Ni)			
	CO Adsorption at 300 K in He	CO Adsorption at 385 K in H ₂		
		30 min	60 min	120 min
19% Ni/Al ₂ O ₃	1020	1760	2470	2530
Al ₂ O ₃ + 19% Ni/Al ₂ O ₃ (dry)	1020	3000	3780	4380
Al ₂ O ₃ + 19% Ni/Al ₂ O ₃ (wet)	590	2850	3400	3850
Al ₂ O ₃ + 9.5% Ni/Al ₂ O ₃ (dry)	220	360	495	—
Al ₂ O ₃ + 9.5% Ni/Al ₂ O ₃ (wet)	115	325	415	—
9.5% Ni/SiO ₂ on Al ₂ O ₃ bed	185	295	—	—

similar to that in Fig. 2a, though the CH₄ signal in Fig. 2b was broader at high temperature. Additional CO adsorbed on the dry mixture when the CO was adsorbed for 120 min at 385 K, as shown in Fig. 3b, and the peak temperature in Fig. 3b was 12 K higher than that in Fig. 3a. The total amount of CH₄ was 4380 μmol/g Ni, which is 1.7 times the amount formed from the catalyst alone. Table 1 summarizes the amounts of CH₄ formed.

The corresponding CH₄ spectra from TPR of CO adsorbed on the 50:50 Al₂O₃-Ni/Al₂O₃ physical mixture (wet) are shown in Figs. 1c, 2c, and 3c. For CO adsorbed in He at 300 K, the CH₄ spectrum (Fig. 1c) is significantly different from that for either the dry mixture or the 19% Ni/Al₂O₃ catalyst alone. The amount of CH₄ formed is only 60% of that observed for the catalyst alone, and the high temperature peak was preferentially smaller. Also, the high temperature peak is at 35 K higher temperature and is broader than the peak for the Ni/Al₂O₃ alone, so that two distinct peaks are clearly observed for the wet mixture. The amount of CH₄ formed during TPR increased when CO was adsorbed in H₂ at 385 K on the wet mixture, and the increase over that adsorbed at 300 K was the same as seen for the dry mixture (Table 1). Thus, much more CH₄ (3850 μmol/g Ni) was seen for the wet mixture than for the 19% Ni/Al₂O₃ catalyst

alone (2530 μmol/g Ni). Near saturation, the CH₄ peak temperature was 22 K higher than that for the catalyst alone and 9 K higher than that for the dry mixture (Fig. 3). The TPR spectra for the wet mixture were dependent on the crushing time while wet, and for mixtures prepared for shorter crushing times, the spectra were more similar to those of the dry mixtures.

A similar set of TPR experiments for a Al₂O₃-Ni/SiO₂ mixture (wet) is shown in Fig. 4. Only one CH₄ site is seen during TPR for CO adsorbed on Ni/SiO₂ catalysts (9, 11), but the TPR spectra for the Al₂O₃-Ni/SiO₂ mixtures (wet) clearly show the presence of two well-defined CH₄ peaks. A small high-temperature CH₄ peak is present for CO adsorption at 300 K, and more CH₄ formed at high temperature for CO adsorption in H₂ (Fig. 4b) than for CO adsorption in He (Fig. 4a). The same dependence on carrier gas during adsorption was seen for Ni/Al₂O₃ catalysts (2, 9). The low-temperature CH₄ peak had essentially the same peak temperature as seen for the 9.5% Ni/SiO₂ catalyst alone, but the peak amplitude (*per gram Ni*) for the mixture was half that of the catalyst alone. That is, as was observed for the Al₂O₃-Ni/Al₂O₃ wet mixture, less CO adsorbed at 300 K in He when the mixture was prepared wet.

For CO adsorption at 385 K on the Al₂O₃-Ni/SiO₂ mixture (wet), the amount of

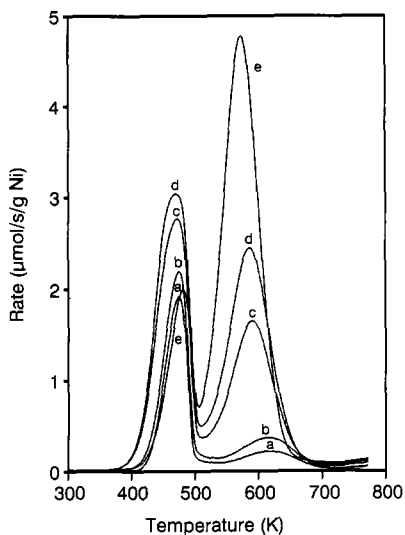


FIG. 4. Methane spectra from TPR of CO adsorbed on a 50:50 physical mixture (wet) of Al_2O_3 and 9.5% Ni/SiO_2 . Gas flowing during adsorption, adsorption temperature, and adsorption time: (a) He, 300 K, 10 min; (b) H_2 , 300 K, 10 min; (c) H_2 , 385 K, 30 min; (d) H_2 , 385 K, 60 min; (e) H_2 , 475 K, 15 min.

CH_4 in the high-temperature peak increased significantly, and the amount of low-temperature CH_4 also increased (Fig. 4c–4d). The low-temperature CH_4 peak, with a peak halfwidth of 61 K, was significantly broader than the low-temperature CH_4 peak obtained for adsorption at 300 K. Most of the increase was on the low-temperature side of the CH_4 peak. The halfwidth of the CH_4 from Ni/SiO_2 alone was 42 K. For adsorption at higher temperature (475 K), but for a shorter time, the high-temperature CH_4 peak was even larger (Fig. 4e), but no indication was obtained that saturation was reached. The CH_4 peak halfwidth after 475 K adsorption was similar to that obtained after 300 K adsorption (42 K). Two separately prepared samples yielded the same results. Note that the amount of additional adsorption on the Al_2O_3 – Ni/SiO_2 mixtures (wet), compared to Ni/SiO_2 alone, was much smaller than the amount of additional adsorption on the Al_2O_3 – $\text{Ni}/\text{Al}_2\text{O}_3$ mixtures, compared to $\text{Ni}/\text{Al}_2\text{O}_3$ alone.

The results were quite different for TPR experiments on the Al_2O_3 – Ni/SiO_2 mixture (dry). Adsorption at 300 K yielded a CH_4 peak that was similar in location and amplitude to that seen on the 9.5% Ni/SiO_2 catalyst alone. A small high-temperature shoulder was observed, however, and a small amount of CH_4 appeared to form at higher temperatures. The CH_4 signal amplitude at temperatures greater than 600 K was barely above the baseline in Fig. 5a. The amplitudes of both the shoulder and the high-temperature peak increased following adsorption at 385 K, but as shown in Fig. 5b, these peaks were significantly smaller than the high-temperature CH_4 peaks from the Al_2O_3 – Ni/SiO_2 mixture (wet). Even after 120 min of CO adsorption at 385 K, the amount of CH_4 formed at high temperature during TPR was small (Fig. 5c).

The CH_4 spectrum obtained from the 9.5% Ni/SiO_2 catalyst resting on top of an Al_2O_3 bed was essentially the same as that obtained from the 9.5% Ni/SiO_2 catalyst alone (9, 11). Only one CH_4 peak was evident, even after CO adsorption at 385 K in

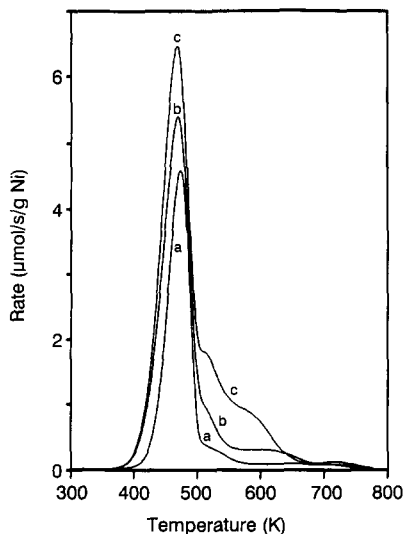


FIG. 5. Methane spectra from CO adsorbed on a 50:50 physical mixture (dry) of Al_2O_3 and 9.5% Ni/SiO_2 . Carbon monoxide was adsorbed in H_2 flow at (a) 300 K (15 min); (b) 385 K (30 min); (c) 385 K (120 min).

H₂ flow. However, after CO adsorption at 385 K, the peak halfwidth increased, and most of the increase was on the low-temperature side of the CH₄ peak. The amounts of CH₄ were quite similar to those observed for Ni/SiO₂ alone.

Note that the peak widths of the low-temperature CH₄ peaks increased for all the mixtures that contained Ni/SiO₂, and the increase was on the low-temperature side. This additional CH₄ may be due to carbon that formed during high-temperature exposure. Since carbon hydrogenates faster than CO, the CH₄ from carbon hydrogenation appears at lower temperature. For adsorption at 475 K, however (Fig. 5e), the low-temperature CH₄ peak was essentially the same as that following 300 K adsorption, apparently because the carbon hydrogenated sufficiently fast that it was all removed before the TPR experiment was carried out.

Temperature-Programmed Desorption

Temperature-programmed desorption, following coadsorption of CO and H₂ on the Al₂O₃-Ni/Al₂O₃ mixture (wet) at 385 K for a

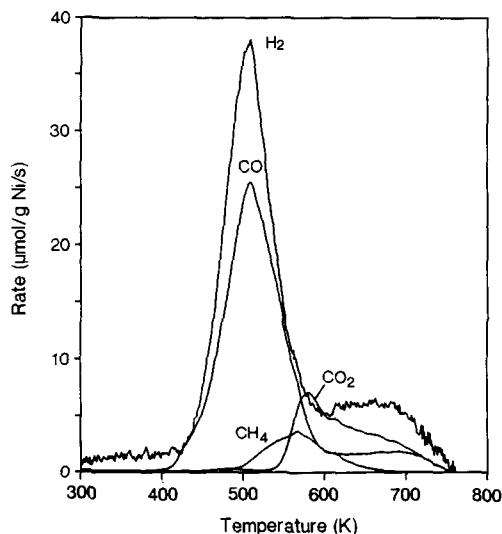


FIG. 6. Desorption product spectra for TPD of CO and H₂ coadsorbed on a 50:50 physical mixture (wet) of Al₂O₃ and 19% Ni/Al₂O₃. The CO was adsorbed in H₂ flow for 120 min at 385 K.

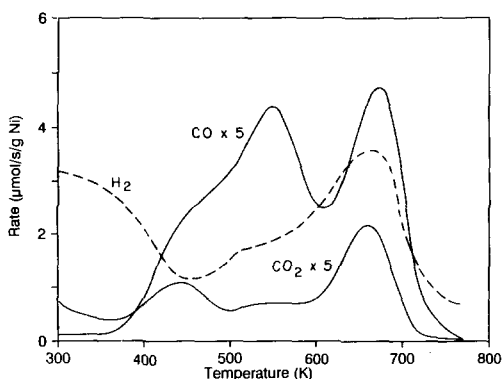


FIG. 7. Desorption product spectra from TPD of CO adsorbed for 30 min in H₂ at 385 K on a 50:50 physical mixture (wet) of Al₂O₃ and 9.5% Ni/SiO₂.

range of coverages, resulted in simultaneous desorption of H₂ and CO (Fig. 6), as observed for the catalyst alone (9). Moreover, more total gas desorbed from the mixture (on a per gram Ni basis) than from the catalyst alone, in agreement with the TPR results. In addition to CO and H₂ desorption, small amounts of CH₄ and CO₂ formed (Fig. 6). Saturation was obtained at a time longer on the mixture than that on the catalyst alone. The peak temperature for H₂ and CO desorption was higher for the mixture than for the catalyst alone, but it was similar to the CH₄ peak temperature observed during TPR for the mixture.

Coadsorption of H₂ and CO at 385 K on the Al₂O₃-Ni/SiO₂ mixture (wet) yielded the spectra shown in Fig. 7. Some H₂ desorbed near room temperature and the rest desorbed with a peak at 660 K. The CO desorption was characterized by peaks at 545 and 675 K, though a significant shoulder was present at 445 K. Small amounts of CO₂ were also formed. The TPD spectra obtained for H₂ and CO adsorption at 300 K were similar to Fig. 7, but the CO desorption peak at 545 K was absent and the total amount of desorbing gases was less, consistent with the TPR results.

The TPD spectra obtained after coadsorbing H₂ and CO at 385 K on the 9.5% Ni/SiO₂ catalyst resting on an Al₂O₃ bed is shown in

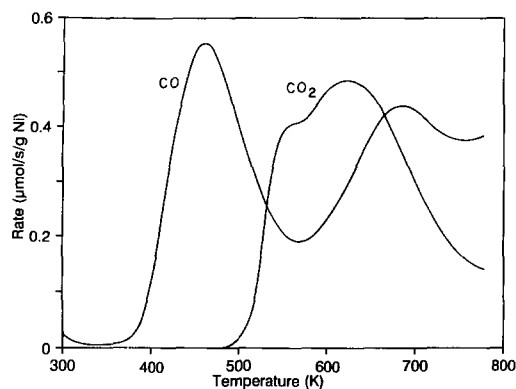


FIG. 8. TPD spectra of CO and CO₂ from 9.5% Ni/SiO₂ (51 mg) resting on a Al₂O₃ bed (50 mg). The CO was adsorbed for 18 min in H₂ at 385 K.

Fig. 8. No H₂ was detected. Coadsorbing CO and H₂ at 300 K and adsorbing CO alone at 300 K gave the same results as those shown in Fig. 8.

DISCUSSION

Two distinct forms of adsorbed CO, corresponding to CO on the metal and as a H-CO complex on the support, have been identified on Al₂O₃- and TiO₂-supported Ni, Ru, and Pt (7-9, 13) with the aid of TPR and TPD. Two forms of adsorbed CO have also been observed on Pt/Al₂O₃ catalysts by TPR combined with IR (5). The TPR and TPD experiments in the present study, on physical mixtures of Al₂O₃ and supported Ni catalysts, confirm that spillover to form a H-CO complex on Al₂O₃ is responsible for the high-temperature CH₄ peak seen in TPR of adsorbed CO on Ni/Al₂O₃ catalysts.

H-CO Complex

The near coincidence of peak temperatures and peak shapes for the H₂ and CO desorbing from the Al₂O₃-Ni/Al₂O₃ mixture (wet), after coadsorbing H₂ and CO at 385 K, and the similarity to the TPD spectra obtained for the 19% Ni/Al₂O₃ catalyst alone (9) suggest the existence of a H-CO surface complex. The H/CO ratio is approx-

imately 3, which is consistent with the stoichiometry of a methoxy species, which has been observed by IR on a Pt/Al₂O₃ catalyst (5). Moreover, the IR results on Pt/Al₂O₃ showed that disappearance of adsorbed CH₃O correlated with formation of CH₄ in one of the TPR peaks (5).

When H₂ and CO were coadsorbed at 385 K on the Al₂O₃-Ni/SiO₂ mixture (wet), a CO desorption peak was observed at 545 K that was not present for coadsorption at 300 K. This peak was also not present for H₂ + CO coadsorption on the 9.5% Ni/SiO₂ catalyst alone (11) or on the 9.5% Ni/SiO₂ catalyst resting on an Al₂O₃ bed. Thus, the CO desorption peak at 545 K cannot be attributed to CO adsorbed on Ni. Moreover, for the Al₂O₃-Ni/SiO₂ mixture, the ratio of H/CO is 2.7 after subtracting the H₂ and CO present on the Ni alone. This result suggests that a H-CO complex with a stoichiometry of 3 may also be present on the physical mixture. The desorption of H₂ and CO from Ni/Al₂O₃ and from the Al₂O₃-Ni/Al₂O₃ (wet) mixture indicates that the complex readily decomposes at high coverages to simultaneously form CO and H₂. However, at low coverages the H₂ and CO peaks do not form simultaneously in TPD on Ni/Al₂O₃ catalysts (14), even though TPR clearly indicates the presence of a high-temperature CH₄ peak. Thus the TPD results on the Al₂O₃-Ni/SiO₂ mixture (wet) should be compared to low coverage TPD results on Ni/Al₂O₃, for which H₂ desorbs before CO, and CO desorption spectra following CO and H₂ coadsorption at 385 K is significantly different from that for CO adsorption at 300 K. Since an increase in adsorption temperature changed the TPD spectra for the Al₂O₃-Ni/SiO₂ physical mixture (wet), but not for the 9.5% Ni/SiO₂ catalyst resting on an Al₂O₃ bed, a H-CO complex apparently forms on the physical mixture but not on either Ni/SiO₂ or Al₂O₃ alone. Thus, we conclude that the H-CO complex is present at low coverages on the Al₂O₃ surface for the Al₂O₃-Ni/SiO₂ (wet) mixture.

TABLE 2

Amount of Adsorbed CH₃O ($\mu\text{mol/g Al}_2\text{O}_3$)

Catalyst	CO Adsorption time at 385 K		
	30 min	60 min	120 min
19% Ni/Al ₂ O ₃	175	340	355
Al ₂ O ₃ + 19% Ni/Al ₂ O ₃ (dry)	210	290	350
Al ₂ O ₃ + 19% Ni/Al ₂ O ₃ (wet)	240	295	345
Al ₂ O ₃ + 9.5% Ni/SiO ₂ (dry)	8	14	—
Al ₂ O ₃ + 9.5% Ni/SiO ₂ (wet)	13	19	—

Evidence for Spillover

Figures 2 and 3 clearly show that, following adsorption at 385 K, more CH₄ is produced *per gram Ni* during TPR for physical mixtures of Al₂O₃ and 19% Ni/Al₂O₃ than for 19% Ni/Al₂O₃ alone. The amounts of CH₄ in the high-temperature peaks in Fig. 3, when normalized *per gram Al₂O₃*, however, were the same for the Al₂O₃-Ni/Al₂O₃ mixtures as for 19% Ni/Al₂O₃ alone (see Table 2). The amount of CH₄ produced in each high-temperature peak was calculated by taking the difference between the total amount of CH₄ produced from CO adsorbed at 385 K in H₂ and the amount of CH₄ produced from CO adsorbed at 300 K in He. At 300 K in He, CO adsorbs only on Ni (7). Thus, when Al₂O₃ was added to the 19% Ni/Al₂O₃, the amount of adsorption *per gram Ni* increased because of the additional support surface available. However, *per gram Al₂O₃*, the amounts of CH₄ produced in the high-temperature peak for the mixtures and for the catalyst alone were almost the same. This is direct evidence that the H-CO complex adsorbs on the Al₂O₃ support.

The concentration of the sites associated with the Al₂O₃ support (as estimated from the amount of CH₄ formed) is 350 $\mu\text{mol/g Al}_2\text{O}_3$ or approximately 1 $\mu\text{mol/m}^2 \text{ Al}_2\text{O}_3$. This value is in good agreement with volumetric methanol adsorption measurements by Rossi *et al.* (15), who deduced a surface concentration of the CH₃O species of 1

$\mu\text{mol/m}^2 \text{ Al}_2\text{O}_3$ on a $\delta\text{-Al}_2\text{O}_3$ support over a temperature range of 298–473 K.

Convincing evidence that the H-CO complex resides on the Al₂O₃ support is obtained from the TPR results for the 9.5% Ni/SiO₂ catalyst physically mixed (wet) with Al₂O₃. On pure Ni/SiO₂, CH₄ forms in a single peak during TPR and this CH₄ is from hydrogenation of CO adsorbed on Ni (9, 11); however, on our Al₂O₃-Ni/SiO₂ physical mixtures (wet), CH₄ formed in two distinct peaks that mimic the TPR behavior of lower weight-loading Ni/Al₂O₃ catalysts (2). The high-temperature peak was smaller on the Al₂O₃-Ni/SiO₂ mixture (wet) than on Ni/Al₂O₃ catalysts (for similar exposures), and thus only a fraction of the Al₂O₃ surface in the mixture was occupied by spillover. The TPR results for the Ni/SiO₂ bed resting on an Al₂O₃ bed and for the Al₂O₃-Ni/SiO₂ (dry) mixture both show that direct adsorption on Al₂O₃ does not make a significant contribution to the amounts adsorbed.

Spillover Mechanism

From the data in Table 1, the rate of spillover (*per gram Ni* in the catalyst or the mixture) increased in the following order:

- Ni/SiO₂ bed on Al₂O₃ bed. No spillover was detected.
- Al₂O₃-Ni/SiO₂ dry mixture. Almost no spillover occurred *during* TPR, but a small amount of spillover was observed during CO adsorption in H₂ flow at 385 K.
- Al₂O₃-Ni/SiO₂ wet mixture. A small amount of CO transferred during TPR and significant coverage of the Al₂O₃ was obtained by CO adsorption in H₂ flow at 385 K. However, the coverage was low compared to the Al₂O₃-Ni/Al₂O₃ mixtures.
- Ni/Al₂O₃ and the Al₂O₃-Ni/Al₂O₃ mixtures. More than half the CO adsorbed on Ni at 300 K transferred during TPR for the Ni/Al₂O₃ catalyst, and the Al₂O₃ support was saturated faster for the Ni/Al₂O₃ catalyst than for the mixtures. Because more Al₂O₃ area was available on the Al₂O₃-Ni/

Al_2O_3 mixtures, however, more spillover occurred (per gram Ni), but a longer time was required for saturation.

The above comparison is per gram Ni, but both the Ni surface area and the Al_2O_3 surface area affect the rate of spillover. As shown in Table 2, the amount of adsorbed CH_3O , per gram Al_2O_3 , is similar for the Ni/ Al_2O_3 catalyst and the mixtures that contain Ni/ Al_2O_3 . At long times, these samples all approach the same saturation value. However, more CH_3O is present for a wet mixture at short times than for the corresponding dry mixture, even though less Ni area is available in the wet mixtures, because contact between particles also affects the spillover rate.

Although a comparison of the samples that contain Ni/ Al_2O_3 catalyst shows that the Al_2O_3 surface area appears to control the amount of spillover for CO adsorption at 385 K, this is not true for the samples that contain Ni/ SiO_2 . The rate of spillover is slower with Ni/ SiO_2 as the source, because CH_3O is not stable on SiO_2 and less Ni surface area is present. When the Al_2O_3 -Ni/ Al_2O_3 and the Al_2O_3 -Ni/ SiO_2 mixtures are compared per unit Ni surface area, the differences in the amount of CH_3O formed at 385 K are only a factor of 3–4 instead of 20–25. Since more spillover occurs on Ni/ Al_2O_3 catalysts with higher Ni loadings (2), the differences between the two types of Ni sources appear to be at least partly due to the differences in Ni surface area.

These results are consistent with spillover being a surface process. Spillover depends on the proximity and the contact of the Ni to the Al_2O_3 . Spillover apparently occurs over relatively short distances, since spillover was observed for the Al_2O_3 -Ni/ SiO_2 mixture (dry), but not for the Ni/ SiO_2 bed resting on an Al_2O_3 bed. Both the dry and the wet mixtures of Al_2O_3 -Ni/ SiO_2 were crushed by the same procedure, and thus the proximity of Ni and Al_2O_3 for these mixtures should be similar, but spillover was faster

for the wet mixtures. Apparently water, by making particles stick together, improves the contact between particles.

Though CH_3O is not stable on SiO_2 , the Ni/ SiO_2 catalyst acted as a source for creating a CH_3O complex on Al_2O_3 . That is, the Al_2O_3 -Ni/ SiO_2 mixture (wet) behaves as a reasonable approximation to a low loading Ni/ Al_2O_3 catalyst. Thus, for both Ni/ Al_2O_3 (2) and the Al_2O_3 -Ni/ SiO_2 mixtures (wet), CO adsorption at 300 K in H_2 results in more high-temperature CH_4 during TPR than that seen for CO adsorption at 300 K in He.

The rate of hydrogenation of the CH_3O species depends significantly on the Ni weight loading (Ni surface area), as shown previously for a series of Ni/ Al_2O_3 catalysts (2). The hydrogenation rate may also depend on the contact between particles and the proximity of Ni and Al_2O_3 , but these effects are difficult to separate from the weight loading effect in the present study. By mixing Al_2O_3 with a supported Ni catalyst, we are essentially creating a lower loading catalyst, i.e., a catalyst with less Ni surface area. Also, as discussed below, crushing the mixtures while wet further decreases the Ni surface area. As shown in Fig. 1, as the Ni surface area decreases in the order,

- (1) 19% Ni/ Al_2O_3
- (2) Al_2O_3 -Ni/ Al_2O_3 mixture (dry)
- (3) Al_2O_3 -Ni/ Al_2O_3 mixture (wet)

the peak temperature for the CH_4 formed from CH_3O hydrogenation increases. This decreased rate of CH_3O hydrogenation with decrease in Ni surface area is clearly shown in Figs. 1–3. For the Al_2O_3 -Ni/ Al_2O_3 mixture (wet), the rate of hydrogenation is even lower, the Ni/ SiO_2 catalyst has only half the Ni loading, and much less Ni surface area, than the Ni/ Al_2O_3 catalysts. This dependence of methanation rate on Ni surface area would be expected if reverse spillover from Al_2O_3 to Ni is necessary for CH_3O hydrogenation, or if H_2 spillover from Ni onto Al_2O_3 is required. In either case, a longer

diffusion distance would result in a lower rate of hydrogenation.

Nickel Surface Area Decrease

When the mixtures of Al₂O₃ and Ni/Al₂O₃ or Ni/SiO₂ were prepared by dry crushing, the amounts of CO adsorbed in He at 300 K were similar in each case to the amounts adsorbed on the individual catalyst, when normalized per gram of Ni. When the mixtures were prepared by wet crushing, however, the amount of CO adsorbed (per gram Ni) decreased to slightly more than half that adsorbed on the catalyst alone (compare Figs. 1a and 1c, and Figs. 4a and 5a). That is, the wet crushing procedure appeared to significantly decrease the available Ni surface area. We do not have an explanation for this behavior but it was observed on two, separately prepared Al₂O₃-Ni/SiO₂ mixtures and one Al₂O₃-Ni/Al₂O₃ mixture. It was not observed on an Al₂O₃-Ni/Al₂O₃ mixture (wet) for which a short crushing time was used.

The locations of the CH₄ peaks for TPR on the Al₂O₃-Ni/Al₂O₃ mixtures were also consistent with this decrease in surface area. As previously discussed, as the Ni surface area decreased, the CH₄ peak due to CH₃O hydrogenation increased in temperature. For the 19% Ni/Al₂O₃ catalyst the high-temperature CH₄ peak had a peak temperature that was close to that for hydrogenation of CO on Ni. For a 5% Ni/Al₂O₃ catalyst, this CH₄ peak temperature was 525 K, and for a 0.74% Ni/Al₂O₃ catalyst it was at 695 K (2). The CH₄ peak due to CH₃O hydrogenation on the Al₂O₃-Ni/Al₂O₃ mixture (wet) in Fig. 1c is at a higher temperature than that for the Al₂O₃-Ni/Al₂O₃ mixture (dry). That is, as the Ni surface area decreased due to wet crushing, CH₃O hydrogenated at a slower rate; this is the same trend observed for Ni/Al₂O₃ catalysts alone and verifies that the Ni surface area was decreased by this preparation. For a short crushing time, the amount of CO adsorption was the same

as that for 19% Ni/Al₂O₃ and the peak temperatures were also similar.

CONCLUSIONS

Temperature-programmed reaction and desorption studies on physical mixtures of supported Ni catalysts and Al₂O₃ demonstrate directly that the high-temperature CH₄ peak observed during TPR (CO hydrogenation) on Ni/Al₂O₃ catalysts is due to hydrogenation of a H-CO species (most likely CH₃O), which is adsorbed on the Al₂O₃ surface. The concentration of CH₃O on Al₂O₃ is approximately 1 μmol/m². The spillover from Ni to Al₂O₃ increased with closer proximity of the metal and support, higher Ni surface area, more available Al₂O₃ surface area, and better contact between particles. The rate of CH₃O hydrogenation increased with Ni surface area. When mixtures were prepared by crushing together support and catalyst while wet, a significant loss in surface area was observed.

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