JOURNAL OF CATALYSIS 74, 199–202 (1982)

Titania-Supported Metals as CO Hydrogenation Catalysts

There is presently much interest in the role of the support in determining the adsorption and catalytic behavior of supported metal systems. Many examples exist which show little or no effect of the support on activity or selectivity in a particular reaction. However, CO hydrogenation represents one reaction which is susceptible to metal–support effects, and both specific activity and selectivity can be markedly influenced by both the metal and the support (1–6). Titania is a metal oxide support which has been found to strongly inhibit chemisorption of H_2 and CO on Group VIII metals after appropriate reduction conditions (7). Regardless, some metals have been found to have their highest activities for CO hydrogenation when dispersed on TiO_2 (2, 4–6). Titania-supported nickel has turnover frequencies one to two orders of magnitude higher than other Ni catalysts and, perhaps more intriguingly, gains the capacity to produce higher-molecular-weight paraffins (2, 8). Platinum on TiO_2 is the most active Pt catalyst (4) and TiO_2-supported Pd is the most active Pd catalyst (5); however, in these two systems selectivities were altered little at atmospheric pressure and methane was essentially the only product. Titania-supported Ru did not exhibit higher activity but showed favorable selectivity shifts toward lower methane make and higher olefin production (3). Rhodium on TiO_2 showed a higher capability to produce olefins but the effect was less pronounced than with Ru (9).

Such favorable trends are not always observed with the Group VIII metals, however, and in some cases catalytic behavior is affected little or in a negative manner. This note compares the adsorption and catalytic properties of the Group VIII metals on TiO_2 after a single, specific pretreatment and under identical reaction conditions. The pretreatment prior to chemisorption measurements or kinetic runs was identical to that used earlier for Al_2O_3-supported metals and consisted of a final 1-hr reduction at 723 K under ~50 $cm^3 \cdot min^{-1}$ flowing hydrogen (10). Product analyses were taken after 20 min on stream at a given temperature and therefore best represent *initial* activities. After each measurement the catalyst surface was cleaned in pure flowing H_2 for 20 min. Details of the experimental systems and procedures have been given already (10). All catalysts were prepared by incipient wetness impregnation using the same metal salts used previously (10) except for the iron catalysts, which were prepared using acetone rather than water. Unless otherwise noted, Cab-O-Ti

TABLE 1

Gas Uptakes (μmol g^{-1}) on Used TiO_2-Supported Metals

Catalyst	CO	$CO_{(ad)}/M$	H_2	$H_{(ad)}/M$
2% Rh	5.0	0.026	0	0
2% Pd	1.0	0.005	18	0.19
1.86% Pd[a]	7.0	0.040	2.0	0.023
2% Ru	7.2	0.036	1.3	0.013
1.53% Ni	55	0.21	1.8	0.014
1.5% Ni[b]	80	0.32	12	0.094
10% Ni	190	0.11	31	0.036
10% Ni[b]	250	0.15	67	0.079
2% Pt	2.6	0.025	0	0
2% Ir	13.4	0.13	2.9	0.056
1.5% Fe	8.3[c]	0.032	0[c]	0
5% Fe	12.7[c]	0.014	6.3[c]	0.014
1.5% Co	9.6	0.037	6.3	0.048

[a] From Ref. (5).

[b] Degussa P-25 titania.

[c] Uptakes on fresh, reduced samples.

0021-9517/82/030199-04$02.00/0

(Cabot Corp.) titania was used as the support.

Table 1 represents CO and H_2 uptakes on the catalysts after the kinetic runs were conducted. All samples were rereduced in H_2 following the standard pretreatment. Except for CO adsorption on 1.5% Ni/TiO_2 and the H_2 uptake on 2% Pd/TiO_2, uptakes of both gases are very low on all catalysts, which strongly infers that the strong metal–support interaction (SMSI) state described by Tauster *et al.* (*7*) still exists. The high H/Pd ratio for the 2% Pd/TiO_2 catalyst is probably due to bulk hydride formation, because it was not corrected for absorption, and it indicates large Pd crystallites. The higher $CO_{(ad)}/H_{(ad)}$ ratios for the 1.5% Ni/TiO_2 catalysts are not unusual for catalysts with low Ni loadings and very small nickel crystallites (*11*, *12*). This behavior has been attributed to subcarbonyl formation on the Ni surface (*13*).

The activation energies and partial pressure dependencies in the methanation reaction are listed in Table 2 and compared to previously reported values for these metals dispersed on alumina. Activation energies, E_{CO}, for CO conversion to all hydrocarbon products are also given. In many cases, E values are quite similar for metals on these two supports; however, significant differences exist for Rh, Co, and especially Fe. With the possible exception of Rh and Co, partial pressure dependencies are not mark-

TABLE 2

Kinetic Parameters over TiO_2- and Al_2O_3-Supported Metals[a]

	$N_{CH_4} = Ae^{-E_m/RT}P_{H_2}^{X}P_{CO}^{Y}$			
Catalyst	E_m (kcal mol^{-1})	X	Y	E_{CO} (kcal mol^{-1})
2% Ru/TiO_2	21.9 ± 2.0	2.0 ± 0.2	−0.5 ± 0.2	19.7 ± 1.3
5% Ru/Al_2O_3	24.2	1.6	−0.6	18.3
1.53% Ni/TiO_2	27.5 ± 1.2	0.9 ± 0.1	−0.3 ± 0.1	26.6 ± 0.9
1.5% Ni/TiO_2[b]	27.0	—	—	27.8
10% Ni/TiO_2	27.2	—	—	31.5
10% Ni/TiO_2[b]	32.4	—	—	27.6
5% Ni/Al_2O_3	25.0	0.8	−0.3	23.5
2% Rh/TiO_2	33.2 ± 1.6	1.7 ± 0.3	−0.1 ± 0.1	32.1 ± 1.4
1% Rh/Al_2O_3	24.0	1.0	−0.2	24.2
2% Pd/TiO_2	22.3 ± 1.2	0.8 ± 0.1	0.2 ± 0.1	22.3 ± 1.2
1.86% Pd/TiO_2	23.6 ± 0.7	0.6 ± 0.1	0.0 ± 0.1	23.6 ± 0.7
2% Pd/Al_2O_3	19.7	1.0	0.0	19.7
2% Pt/TiO_2	16.8 ± 3.9	0.5 ± 0.1	0.2 ± 0.1	14.7 ± 3.3
1.75% Pt/Al_2O_3	16.7	0.8	0.0	15.3
2% Ir/TiO_2	23.2 ± 0.7	1.0 ± 0.1	−0.3 ± 0.1	25.3 ± 1.0
2% Ir/Al_2O_3	16.9	1.0	0.1	11.7
1.53% Co/TiO_2	17.8 ± 3.9	1.8 ± 0.4	0.0 ± 0.2	18.2 ± 4.3
2% Co/Al_2O_3	27.0	1.2	−0.5	26.7
1.46% Fe/TiO_2	6.1 ± 0.6	—	—	—
5% Fe/TiO_2	4.7 ± 2.4	—	—	—
15% Fe/Al_2O_3	21.3	1.1	−0.1	25.9

[a] Results for Al_2O_3-supported metals from Ref. (*10*), $H_2/CO = 3$, $P = 101$ kPa.

[b] Degussa P-25 titania.

TABLE 3

Activity Comparisons of Supported Metals

Catalyst	Activity (μmol CO · s^{-1} · g $metal^{-1}$)	N_{CO} at 275°C ($s^{-1} \times 10^3$)	
2% Ru/TiO_2	120	320[a]	12[b]
5% Ru/Al_2O_3	190	325	—
1.53% Ni/TiO_2	270	75	16
1.5% Ni/TiO_2[c]	720	130	41
10% Ni/TiO_2	1530	820	90
10% Ni/TiO_2[c]	830	330	50
5% Ni/Al_2O_3	84	38	—
2% Rh/TiO_2	110	430	11
1% Rh/Al_2O_3	80	17	—
2% Pd/TiO_2	5	100	0.50
1.86% Pd/TiO_2	10	27	1.1
2% Pd/Al_2O_3	14	13	—
2% Pt/TiO_2	17	130	3.4
1.75% Pt/Al_2O_3	8	3.4	—
2% Ir/TiO_2	30	45	5.8
2% Ir/Al_2O_3	6	2.6	—
1.53% Co/TiO_2	13	20	0.70
2% Co/Al_2O_3	20	28	—
1.46% Fe/TiO_2	0.13	0.02	0.0007
5% Fe/TiO_2	0.09	0.03	0.005
15% Fe/Al_2O_3	23	160	—

[a] Based on $CO_{(ad)}$ from Table 1 and from Ref. (*10*).
[b] Assuming 100% dispersion.
[c] Degussa P-25 titania.

edly affected by the support. Values for Fe could not be determined because of the extremely low activity.

The most apparent differences between the TiO_2-supported metals and those on a typical support like η-Al_2O_3 appeared in activity, as shown in Table 3. A comparison of turnover frequencies (TOF) based on adsorbed CO, assuming an adsorbed CO molecule defines an "active site," shows that TOF values are higher on Ni, Rh, Pd, Pt, and Ir, comparable on Ru and Co, but four orders of magnitude lower on Fe. However, monolayer coverages of CO and hydrogen are markedly decreased on TiO_2-supported metal surfaces and may not be expected to be an accurate measure of the total metal surface area (*7, 11, 12*). If a limiting assumption is made of 100% metal dispersion on TiO_2, which produces the minimum TOF possible, it is clear that many of these TiO_2-supported metals, such as Ni, Pd, Pt, Rh, and Ir, still have comparable or higher specific activities. However, values for Ru, Co, and Fe are much lower on this basis. The assumption of high dispersion is probably quite valid for the Ru/TiO_2 catalyst as XRD results showed no detectable peaks for Ru (*3*); however, Co and Fe are not expected to be well dispersed and their behavior may reflect a greater difficulty in reducing these metals. Regardless, CO is expected to chemisorb on reduced Co and Fe surfaces and appears to count "active sites" on TiO_2-supported Co in a consistent manner. The markedly different behavior of Fe on TiO_2 is exhibited not only by the much lower TOF values but also by the significantly lower activation energies reported in Table 2. Unique SMSI behavior involving both Fe spreading on the titania surface and diffusing into the support has recently been reported for Fe/TiO_2 systems (*14*) and, at this time, the unusual catalytic properties of Fe/TiO_2 are attributed to this interaction. Finally, if activity is compared on a gram metal basis, as in Table 3, the positive influence of TiO_2 is again quite apparent for nickel, while activities are somewhat higher for Ir and Pt, comparable for Ru, Rh, Pd, and Co, and again much lower for Fe. It is important to note that the higher activities are not a consequence of a lower activation energy. Comparable or higher activation energies exist for every TiO_2-supported metal except for the two least active metals, Co and Fe.

In summary, the use of TiO_2 enhances specific activity for CO hydrogenation over the metals which tend to have more completely filled *d* bands (Ni, Pd, Pt, Rh, Ir), has little effect on Ru and Co, and inhibits the TOF on Fe present at low loadings. A similar, but less pronounced, pattern exists for activity on a gram metal basis (in acknowledgment of the difficulty in determining actual metal surface areas in SMSI catalysts). The increase in activity may be the result of higher surface concentrations of hydrogen *under reaction conditions* (*5*), or it may be that this SMSI effect facilitates the CO dissociation step since nondissociative CO adsorption is favored on the more noble metals (*15*). Fewer differences show up in kinetic parameters for the methanation reaction, and partial pressure dependencies are not markedly changed by the use of titania, in general. It is apparent that the use of TiO_2 as a support can alter the adsorption and catalytic properties of the metal–support system, presumably via electron transfer as a consequence of a strong metal–support interaction (*16*). However, the consequences of this interaction can vary markedly from metal to metal.

ACKNOWLEDGMENTS

Many of these results were obtained at the Corporate Research Laboratories, Exxon Research and Engineering Company. The assistance of Miss Donna Piano is gratefully acknowledged.

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Received August 14, 1981; revised November 19, 1981