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Effects of Variation of Electric Properties of TiO_2 Support on Hydrogenation of CO and CO_2 over Rh Catalysts

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The catalytic activity of Rh in the hydrogenation of CO and CO_2 has been investigated as a function of the electric properties of the *n*-type TiO_2 support. The latter were altered by doping the TiO_2 with lower and higher valency cations. It was demonstrated that variation of the electric conductivity of the TiO_2 influences the catalytic performance of the Rh. The turnover frequency of methane formation increased significantly due to the incorporation of W^{6+} ions into the TiO_2, which increased its electric conductivity by one to two orders of magnitude. Doping with lower valency ions (Mg^{2+}, Al^{3+}), which hardly influenced the electric conductivity of the TiO_2 support, caused only little alteration in the specific activity of the Rh. It was shown that the disproportionation of CO on Rh is affected in the same direction by the doping of the TiO_2 support. The favorable effect of doping with the W^{6+} ion is attributed to the enhanced electron transfer from the TiO_2 to the Rh, which promotes the dissociation of CO. The results are considered to be evidence of the occurrence and the role of the electronic interaction between the metal catalyst and the titania support.

INTRODUCTION

It has long been recognized that supports not only provide a high surface area for metal catalysts, but also drastically modify the catalytic properties of the metals. Several types of interactions have been proposed and demonstrated experimentally (*1*, *2*).

One of the most controversial explanations was that there is an electronic interaction at the metal–support interface which influences the catalytic performance of the metal. This concept was based on the finding that an electronic interaction develops between two solids with different Fermi electron levels.

The first deliberate attempt to demonstrate the role of this kind of electronic interaction was made by Schwab *et al.* (*3*) using an alumina support. Although they interpreted their results as evidence of the importance of the electronic interaction, their data can hardly be considered as proof of this idea. The electric conductivity of the insulator alumina can be influenced only slightly, if at all, by doping (*3*, *4*). Thus, one can hardly expect any variation in the electric properties of the metal catalyst due to the very limited, if any, electron transfer between the alumina support and the metal. The very low change found in the activation energies of the decomposition of HCOOH on the catalyst (±10%, ±2.5 kcal/mol) (*3*) is in harmony with this consideration.

Szabó and Solymosi (*5*) investigated the decomposition of HCOOH on NiO at that time and observed that, due to the reducing effect of HCOOH (or H_2), a very thin Ni layer was formed on a NiO pellet sintered at 1273 K. The low activation energy of dehydrogenation of HCOOH (~10 kcal/mol) was attributed to the occurrence of an electronic interaction between Ni and *p*-type NiO, electrons flowing from the Ni to the *p*-type NiO at the interface. An attempt was made to prove this suggestion by changing the positive-hole density of the NiO by doping it with Li^+ and Cr^{3+} ions (*5*, *6*).

The efficiencies of doped and undoped *n*-

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type TiO_2 and *p*-type Cr_2O_3 as supports for Ni catalysts were also examined in HCOOH decomposition (7). It was concluded that an electronic interaction exists between Ni and titania, electrons being transferred from the titania to the Ni (7).

Unfortunately, at that time no reliable method was available for selective determination of the surface area of the metal, and therefore all the above findings and conclusions were based on the variation of the activation energy of the reaction.

The surface areas of metals are now routinely determined, and it is therefore tempting to examine whether the electric conductivity of TiO_2, or the Fermi level of the electrons, has any influence on the specific activity of the metal.

For this purpose we chose Rh metal, as we had observed that Rh/TiO_2 reduced at or below 673 K exhibits exceptionally high activity in the formation of surface isocyanate in the NO + CO reaction (*8*), in the methanation of CO_2 (*9*) and CO (*10*), and also in the dissociation of CO (*11*).

EXPERIMENTAL

Materials

BDH TiO_2 was used as the basic material for the support. Its doping was performed in the following way: finely ground TiO_2 was introduced into a solution of the dopant ($(NH_4)_{10}[W_{12}O_{40}(OH)_2] \cdot 4H_2O$, $Mg(NO_3)_2$, and $Al(NO_3)_3$), which was dried at ~355 K during continuous stirring under an infrared lamp. After extensive homogenation, the solids were treated in air at 1073 K for 5 hr and, after grinding, at 1273 K, again for 5 hr. This high-temperature treatment is required for incorporation of the foreign ions into the TiO_2.

These supports were pulverized and impregnated with a solution of $Rh(NO_3)_3 \cdot 2H_2O$ or $RhCl_3 \cdot 3H_2O$ to yield a nominal 1 or 5 wt% Rh metal. The impregnated samples were dried at ~355 K in a similar way as described above. Further treatment was applied *in situ*; it consisted of oxidation of the samples at 673 K and reduction at 573 K for 30 min, and then cooling to the temperature of the experiments in a H_2 flow.

The gases used were of commercial purity. They were carefully purified by adsorbing the impurities with a molecular sieve at the temperature of liquid air. The He was deoxygenated with an "Oxy-Trap" and "Indicating Oxy-Trap" (Altech Co.).

Methods

The dispersity of the supported Rh was determined by H_2 chemisorption at 298 K.

Catalytic measurements were carried out in a flow microreactor made from an 8-mm-i.d. Pyrex glass tube. Its length was 100 mm. The dead volume was filled with glass beads. The reactor was heated by an external oven. A small glass tube containing an Fe–Ko thermocouple was placed in the middle of the catalyst bed. No increase in the catalyst temperature was observed during the reaction. The amount of catalysts used was 0.3–0.6 g. The ratios of H_2/CO and H_2/CO_2 in the reacting gas mixture were in general 3/1 and 4/1, respectively. Helium was used whenever a diluent was needed. Analyses of the exit gases were performed with a Hewlett–Packard 5750 gas chromatograph equipped with a 3370 electronic digital integrator and with a Chrom-4 gas chromatograph. An effluent splitter in the gas chromatography permitted simultaneous detection by thermal conductivity and flame ionization detectors. A 2-m-long, 0.25-in.-diameter column packed with Porapak QS allowed complete separation and determination of reactants and products.

The system was operated at a total pressure of 1 atm. High space velocities of 3000–6000 hr^{-1} were used. The CO or CO_2 conversion was in general less than 5–10%. The absence of diffusional limitation was confirmed.

RESULTS

Hydrogenation of CO

As experienced previously (*10*), the cata-

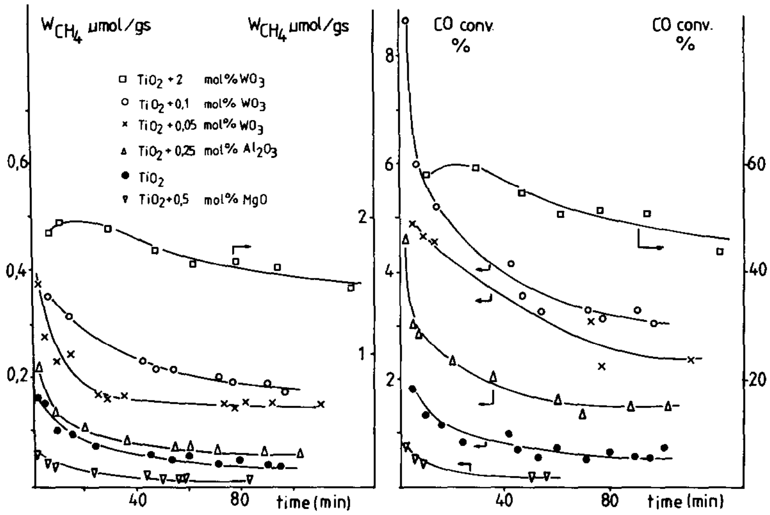

FIG. 1. Changes in the activity of doped and undoped Rh/TiO_2 in the H_2 + CO reaction at 573 K. (●) TiO_2, (X) TiO_2 + 0.05 mol% WO_3, (○) TiO_2 + 0.1 mol% WO_3, (□) TiO_2 + 2 mol% WO_3, (△) TiO_2 + 0.25 mol% Al_2O_3, and (▽) TiO_2 + 0.5 mol% MgO.

lytic activity of Rh/TiO_2 in the hydrogenation of CO greatly decreased in time, and therefore the initial and steady-state activities were determined.

We first investigated the H_2 + CO reaction over Rh deposited on a pure TiO_2 support sintered at 1273 K. These samples were prepared from $Rh(NO_3)_3$. A well measurable reaction was observed on this sample at 573 K (Fig. 1). The initial conversion of CO was 1.5–2%, which decreased with time, and a constant activity (~0.5% CO conversion) was reached in 60 min. The main products were CH_4 and CO_2 together with ethane, ethylene, propane, *n*-butane, and *i*-butane (Fig. 2). During the conditioning period, the selectivity of CH_4 formation was 80–67%. Very similar behavior was observed for the sample Rh/TiO_2 + 0.25% Al_2O_3 and on Rh/TiO_2 + 0.5% MgO; the product distribution differed only slightly (Fig. 2).

A much higher initial CO conversion was observed when the TiO_2 support was doped with WO_3. As can be seen in Fig. 1, on the incorporation of even as little as 0.05% WO_3 into the TiO_2, the production of CH_4 was appreciably larger than when the un-

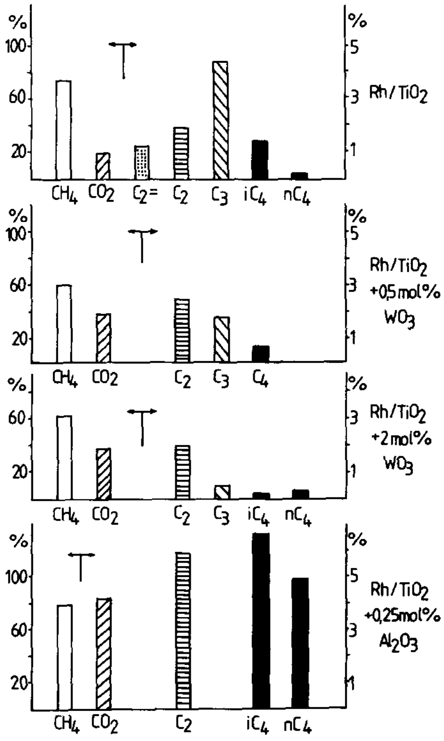

FIG. 2. Product distribution in the hydrogenation of CO on various Rh/TiO_2 samples at 573 K.

doped TiO_2 support was used, and the performance of the catalyst was further improved by increase of the concentration of the W^{6+} dopant. The relative amount of CO_2 increased with the rise of WO_3 content and as a result the selectivity of CH_4 formation decreased. The other products were qualitatively the same as on Rh/TiO_2 (Fig. 2).

The specific activities of the catalysts (in terms of turnover frequencies) were calculated by taking into account the dispersity of Rh on different samples. These values are presented in Table 1. As the dispersity of the Rh varied only slightly in the different samples, the activity sequence of the catalysts remained the same as exhibited in Fig. 1.

The activation energy of methanation was determined for all samples; values of 23–36 kcal/mol were obtained (Table 1).

Some of the experiments were repeated with TiO_2 impregnated in a solution of $RhCl_3$ instead of $Rh(NO_3)_3$. The samples thereby obtained behaved similarly to the previous ones, with the difference being that they underwent a more significant activity decay during the conditioning period.

In order to estimate a contribution to the catalytic effect by the WO_3-doped TiO_2 support, we performed two series of control measurements. In the first, we found that neither pure TiO_2 nor doped TiO_2 supports exhibited a catalytic effect in the hydrogenation of CO up to 623 K. In the other series, we measured the H_2 + CO reaction on reduced WO_3 deposited on TiO_2. In this case, TiO_2 (sintered at 1273 K) was impregnated in a solution of $(NH_4)_{10}[W_{12}O_{40}(OH)_2] \cdot 4H_2O$ dried at 355 K, decomposed, oxidized at 673 K, and reduced at 573 K, in a similar way as the Rh/TiO_2 was prepared. The difference was that in this case—due to the lower temperature—WO_3 could not be

TABLE 1

Summary of the Kinetic Data for the Hydrogenation of CO and CO_2 on Supported Rh Catalysts[a]

Support	Area of the support[b] (m^2/g)	Rh dispersion[b] (%)	H_2 + CO reaction			H_2 + CO_2 reaction		
			N_{CH_4} ($\times 10^3$)	S_{CH_4} (%)	E (kcal/mol)	N_{CH_4} ($\times 10^3$)	S_{CH_4} (%)	E (kcal/mol)
			at 573 K			at 573 K		
TiO_2	8.3	7.84	5.38	57.8	36.2	9.18	30.4	24.6
			6.30	46.4	—			
TiO_2 + 0.05% WO_3	8.8	16.7	9.67	83.6	36.8	11.5	46.0	23.0
TiO_2 + 0.1% WO_3	9.4	16.0	13.0	74.0	32.5	21.8	53.1	22.1
TiO_2 + 2% WO_3	6.8	16.9	89.2	50.1	—	89.6	88.2	17.4
			73.8	60.2	25.7			
TiO_2 + 0.25% Al_2O_3	8.6	22.9	2.96	78.5	30.7	—	—	—
TiO_2 + 0.5% MgO	—	6.9	2.07	71.9	23.4	4.9	27.7	25.0
TiO_2[c]	—	4.4	17.7	90.9	33.4	19.1	49.3	22.0
						12.8	40.1	
TiO_2 + 2% WO_3[c]	—	16.0	67.5	56.4	—	54.9	76.7	17.0
			53.8	59.2	26.7			

[a] Kinetic measurements were performed in general at 573–523 K, with the exception of Rh/TiO_2 + 2 mol% WO_3, when the temperature range was 548–510 K. The conversion of CO and CO_2 varied between 0.2 and 9%.

[b] The Rh content was 1 wt%. The surface area of the support was determined by the BET method. The surface area of TiO_2 (BDH) before thermal treatment was 15.3 m^2/g. The dispersity of Rh was determined after the catalytic measurements.

[c] The Rh was obtained from $RhCl_3$.

TABLE 2

Amount of Surface Carbon Transformed into CH_4 (in μmol/g Catalyst) in the Reaction with H_2 on Rh/TiO_2 Samples at Different Temperatures[a]

Catalyst	573 K	623 K	673 K	723 K	Total amount
TiO_2	3.81	3.92	7.78	4.07	19.58
TiO_2 + 0.5 mol% WO_3	8.21	6.03	11.45	7.14	32.38
TiO_2 + 2 mol% WO_3	22.31	11.92	6.41	3.42	44.06

[a] Surface carbon was formed by the H_2 + CO reaction on reduced Rh samples at 573 K for 60 min, then the reactor was flushed with a He stream for 10 min to remove all the chemisorbed species. Afterward the samples were exposed to H_2 stream. After cessation of CH_4 formation, the reaction temperature was increased.

incorporated into the TiO_2, and was present in a reduced form on its surface. Again we observed no measurable reaction at 473–623 K, and accordingly this amount of tungsten oxides does not catalyze the hydrogenation of CO.

In the subsequent measurements we determined the amount of carbon produced on the catalyst surface during the reaction. In this case all the catalyst samples were treated with the reacting gas mixture at 573 K for 60 min, and they were then flushed with He at the same temperature for 10 min, which was found to be sufficient to remove all the chemisorbed species from the surface (*9*, *10*). Afterward, H_2 was led through the catalyst bed, and the CH_4 (or other hydrocarbons) was determined. When CH_4 formation ceased, the temperature was raised to hydrogenate the less reactive carbon too. The results obtained are presented in Table 2.

A larger amount of carbon was found when the TiO_2 was doped with WO_3; its amount increased with the rise of the WO_3 concentration in the TiO_2.

Hydrogenation of CO_2

The importance of the electric properties of the TiO_2 support was tested in the catalytic hydrogenation of CO_2. From among the Pt metals, Rh was found to be the most effective catalyst in this reaction (*9*, *13*).

The hydrogenation of CO_2 occurred at lower temperatures than that of CO and produced CH_4 and CO. In most cases only a slight activity decrease was experienced. The rate of CH_4 production was the highest again on Rh/TiO_2 doped with WO_3 (Fig. 3). In contrast to our previous results on Rh dispersed on Degussa TiO_2 of high surface area (*9*), when the selectivity of CH_4 production was 95–98%, in the present case it

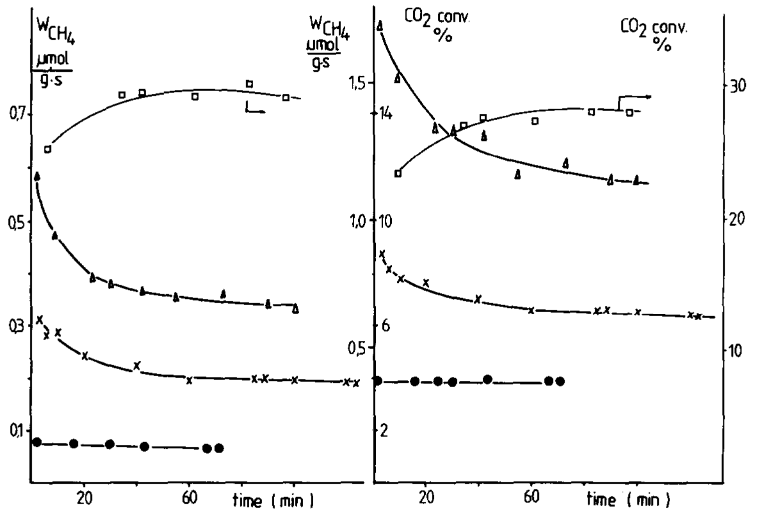

FIG. 3. Changes in the activity of doped and undoped Rh/TiO_2 in the H_2 + CO_2 reaction at 573K. (●) TiO_2, (x) TiO_2 + 0.05% mol% WO_3, (△) TiO_2 + 0.1 mol% WO_3, (□) TiO_2 + 2 mol% WO_3.

varied in the range of 30–90%. The activation energy agreed quite well with those reported for this reaction (*9*) and varied only slightly with the doping of the TiO_2 (Table 1).

Disproportionation of CO

There is a certain controversy in the literature regarding the dissociation of CO on Rh surfaces under UHV conditions. We demonstrated first that the reaction occurs to a well measurable extent at elevated temperatures on supported Rh (*11, 12*). Since the hydrogenation of CO on supported Rh consists of its dissociation and the subsequent hydrogenation of the surface carbon (*10*), it was important to examine the effects of different TiO_2 samples on these processes.

In these experiments a gas mixture of He + CO (containing 25% CO) was passed through the reduced Rh samples and the CO_2 formed in the disproportionation reaction was determined continuously. After 60 min, the gas mixture was replaced by He, and then with H_2, and the amount of surface carbon was measured in a similar way as before. As the data presented in Fig. 4 show, the disproportionation of CO on Rh/TiO_2 is influenced by the doping of the TiO_2. The incorporation of W^{6+} ions into the TiO_2 markedly increased the evolution of CO_2, while doping of the TiO_2 with ions of lower valency exerted practically no (TiO_2 + 0.25% Al_2O_3) or only a decreasing effect (TiO_2 + 0.5% MgO). The rate of CO_2 formation declined quickly on the tungsten-doped catalysts, too, but even in the pseudo steady state it was higher than on the other Rh/TiO_2 samples. The effects of doping of the TiO_2 support on the turnover frequencies of CH_4 production in the H_2 + CO and H_2 + CO_2 reactions at 573 K are shown in Fig. 5.

DISCUSSION

Rh/TiO_2 has been found to be an effective catalyst in the hydrogenation of CO_2 (*9*) and CO (*10, 14–17*) as well as in the dissociation of CO (*11*).

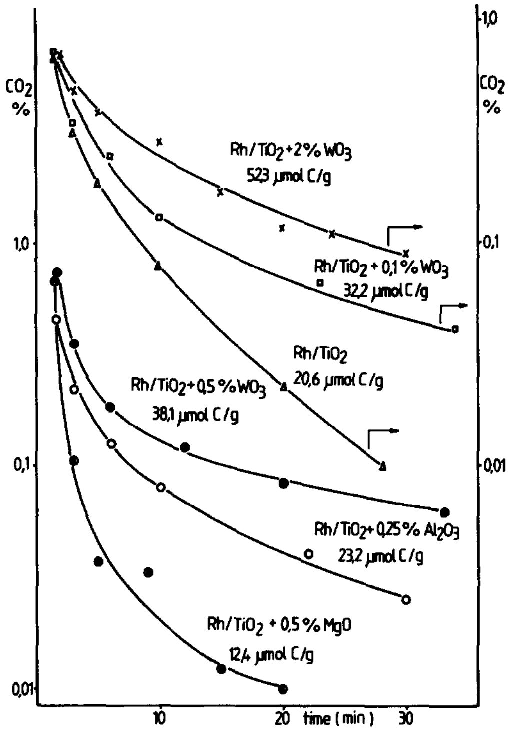

FIG. 4. Disproportionation of CO on various Rh/TiO_2 samples at 573 K. The CO content of He carrier gas was 25%. The total amount of surface carbon formed in 60 min is also shown.

Its high catalytic efficiency was exhibited in the present case too when Rh was deposited on TiO_2 sintered at 1273 K. However, the turnover frequency of CH_4 formation on this sample was about one order of magnitude less than the value reported previously for 1% Rh/TiO_2 (Degussa TiO_2 of high surface area), otherwise determined under exactly the same conditions. Reduction of Rh/TiO_2 samples at 777–873 K led to a loss of their catalytic performance (*10*).

The catalytic performance of the Rh slightly changed when the TiO_2 support was doped with lower-valency ions (Mg^{2+}, Al^{3+}). *However, a drastic increase in the turnover frequency of CH_4 formation was experienced when the support was doped with W^{6+} ions.* The favorable effect of doping the TiO_2 with higher-valency ions ap-

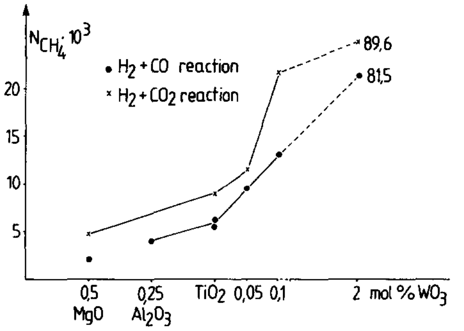

FIG. 5. Effects of doping of the TiO_2 support on the specific activity of Rh (in terms of turnover frequency, molecules formed (or reacted) per metal site × sec) at 573 K.

peared in the disproportionation of CO, too.

Before discussing these results, we should briefly outline the semiconducting properties of TiO_2. Titania is an *n*-type semiconductor; it contains a metal excess, or more correctly anion vacancies (*4, 18*). The characteristics of an *n*-type semiconductor is that its electric conductivity is increased on the incorporation of higher-valency ions into its lattice, the opposite effect being displayed by lower-valency ions. These phenomena can be described by the following defect site reactions (*4*):

$$WO_3 \rightleftharpoons W(Ti)^{2+} + 2e^- + TiO_2 + \tfrac{1}{2}O_2$$

$$Al_2O_3 + 2e^- + \tfrac{1}{2}O_2 \rightleftharpoons 2Al(Ti)^- + 2TiO_2.$$

The electric conductivities of pure and doped TiO_2 have been measured by a number of workers (*4, 18–20*). The results unambiguously showed that the W^{6+} ion increased the conductivity of TiO_2 at most by approximately two orders of magnitude. The lower-valency ions (Al^{3+}, Ga^{3+}, Ni^{2+}, etc.) exerted much smaller effects; the decrease in the conductivity did not exceed 20–30%, if it occurred at all. This is not an unusual feature and it has been observed in several other cases (*4*). The possible reasons are the restricted incorporation of dopant ions, changes in the mobility of the electrons, etc.

What will be the consequences of this change for the Rh/TiO_2 catalyst?

According to the Schottky theory (*21*) of metal/semiconductor contacts at thermodynamic equilibrium, the Fermi levels of the electrons must be the same on both sides of the interface. If the work function of the electrons in the metal is larger than that of those in the semiconducting support, electrons flow from the semiconductor into the metal until equilibrium is attained, and vice versa. As the work function of electrons is in most cases larger in metals than in semiconductors (for instance, the work function of reduced titania Ti^{3+} is 4.6 eV (*22*) while those of Ni and Rh are 5.2 and 4.98 eV (*23*), respectively): electrons are transferred from the semiconductor into the metal. *We assumed the occurrence of this process in Ni/TiO_2 in 1960 and attributed the changes in the catalytic effect of Ni* (*observed as a result of the alteration of the Fermi level in TiO_2*) *to the different extents of electron transfer between Ni and TiO_2* (*7, 2*).

Using a modern electron spectroscopic method, Kao *et al.* (*24, 25*) recently *confirmed not only our view as to the occurrence of the electronic interaction between Ni and TiO_2, but also the direction of the electron flow* we had concluded from the effects of doping the TiO_2 support (*7*). (It is regrettable that they made no mention at all that we had investigated the catalytic behavior of Ni/TiO_2 as a function of the electric conductivity of TiO_2 support and had already reached the conclusions which they confirmed.)

The exceptionally high specific activity of Rh/TiO_2 in the methanation of CO_2 and CO could be explained in a similar way as suggested first by Szabó and Solymosi (*2, 7*) for the Ni/TiO_2 catalyst. We assumed that an electron transfer occurs from the reduced TiO_2 to the Rh, which increases the electron donation from Rh into an antibonding π-orbital of the CO, thereby strengthening the Rh–C bond and weakening the C–O bond (*9, 10*). This model of electronic interaction was also used by Meriadeau *et al.* (*17*) in the explanation of the favorable effect of TiO_2 support for Rh catalysts. In a search to detect some effect of this electronic interaction on the bonding of CO to Rh, we found that the absorption band due to terminal CO appeared at a lower frequency and the dissociation of CO occurred at a somewhat higher rate on Rh/TiO_2 than on other Rh samples (*11*).

The fact that the alteration of the electron concentration (Fermi level of electrons) in TiO_2 influences the specific rate of methanation on Rh/TiO_2 lends support to our idea that this reaction and the catalytic efficiency of the Rh catalyst are sensitive to the electric properties of the support, and to the degree of electronic interaction between the Rh and TiO_2.

Furthermore, the changes in the specific activity of the Rh on variation of the electric properties of the TiO_2 seem to be in harmony with the above explanation. An increase in the electron concentration in the TiO_2 support by WO_3 doping can further enhance the amount of electrons transferred from TiO_2 to Rh, thereby promoting the dissociation of CO on the Rh. The fact that doping of the TiO_2 with Al^{3+} or Mg^{2+} ions influenced the catalytic activity of the Rh only slightly is not in contradiction with this picture, as these ions hardly influence the electric conductivity of TiO_2 either, and thus a large alteration in the catalytic properties of Rh is not to be expected.

The assumption that the favorable effect of titania on the catalytic performance of Rh can be attributed to the promotion of CO dissociation on the Rh is further supported by the results obtained in the study of CO disproportionation on these supported Rh samples. This occurred at a higher rate on Rh deposited on TiO_2 doped with WO_3 (Fig. 4) as compared to other Rh/TiO_2 samples.

In a search for alternative explanations for the enhanced activity of Rh deposited on WO_3-doped TiO_2, one could argue that the incorporation of the W^{6+} ion into TiO_2 accelerates or induces a reaction between Rh and reduced titania, producing a more active catalyst. Another possibility is that in this way the titania support becomes more active for the reaction (as a result of the cooperative effect of Rh and doping with WO_3); i.e., certain steps of the hydrogenation reaction should occur on the surface of the reduced titania support. This possibility of the activation of the support was taken into account in the early works dealing with the effect of titania and other effective supports (*2, 26*), and this idea is currently receiving increasing attention. However, we obtained no evidence for these routes of enhanced activity. As the titania support doped with WO_3 remained practically inactive in the hydrogenation reaction under the experimental conditions applied, even when it had been reduced at a higher temperature, 773 K, it is very unlikely that it could participate directly in the catalysis to such an extent as to account for the enhanced catalytic effect.

One could further speculate that in the course of the catalytic reaction (or during the reduction of the catalyst), the Rh interacts with the unincorporated WO_3, or forms a compound with it which exhibits a much higher activity. A similar interpretation was proposed by Szabó and Solymosi (*2, 6, 7*) for the high efficiency of the Ni/Al_2O_3 + 5% NiO catalyst (observed by Schwab *et al.* (*3*)) compared to the Ni/Al_2O_3 catalyst. It was assumed that the undissolved NiO on Al_2O_3 interacted strongly with the Ni producing a much more effective catalyst than Ni/Al_2O_3 (*6, 7*). A separate study of the catalytic performance of the Ni/NiO catalyst confirmed this assumption (*5, 6*). Although we cannot completely exclude this possibility in the present case, particularly when we used 2 mol% WO_3 as a dopant, it must be pointed out that the doping of the TiO_2 with even a very small amount of WO_3 (0.05 mol%) exerted a well-observable promoter effect, and any "significant" amount of unincorporated WO_3 is hardly to be expected at such a level of dopants.

CONCLUSIONS

(i) A variation of the electron concentration of the TiO_2 support by doping it with altervalent ions influences the specific activity of the Rh catalysts in the hydrogenation of CO and CO_2.

(ii) This effect is attributed to the occurrence of an electronic interaction between Rh and reduced titania support.

(iii) In the interpretation of the high efficiency of the support, TiO_2 + 2 mol% WO_3, a contribution of an interaction or reaction between the Rh and unincorporated WO_3 producing an active phase is proposed.

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