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Frequency Response Study of the Effect of Alkali Promotion on Rh/TiO2 Catalysts: Evidence for Kinetically Distinct H2-Sorbing Sites

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The role of support and alkali promoter on the kinetics of hydrogen chemisorption on supported rhodium catalysts has been investigated using frequency response chemisorption (FRC). In all catalysts studied, several kinetically distinct chemisorbing sites were observed; with the exact number and kinetic parameters depending on the exact combination of promoter and support used. Comparison of the FRC spectra of Rh/SiO_2 and Rh/TiO_2 revealed the existence of new chemisorbing sites in the latter. One of the Rh/TiO_2 sites may be attributed to H_2 spillover onto the support. The addition of alkali promoters suppressed the H_2 chemisorption of specific sites.

INTRODUCTION

The roles of supports and promoters in metal catalysis have been the subjects of study for many years. Although in some instances supports can be considered to be inert substrates, serving only to disperse the metal and increase its surface area, the specific type of support used can have a drastic effect in a catalytic reaction. This is well illustrated in the case of group VIII metals supported on titania, where reduction of the catalyst at high temperature results in a suppression of the normal hydrogen chemisorption, as well as changes in its catalytic behavior toward reactions such as ethane hydrogenolysis and CO hydrogenation. These effects have been attributed to "strong metal–support interactions" (SMSI) (*1–3*). Alkali metal promoters can also have dramatic effects on the activity and selectivity of group VIII metals for CO hydrogenation reactions, where they have been shown to enhance the formation of long-chain hydrocarbons (*4–6*).

Many studies have been reported on the cause of SMSI on supported metal catalysts. Current evidence indicates that the effect is largely the result of migration of support species onto the surface of the metal crystallite, resulting in geometric and electronic perturbation to the site activity (*7, 8*). The influence of these "support-islands" on the kinetics and mechanism of chemisorptive and reactive processes is less clear, although H_2 chemisorption studies have indicated that the suppression phenomenon is a kinetic, rather than thermodynamic effect. Hydrogen desorption after prolonged exposures corresponds reasonably well with the expected metal surface area (*9*).

The cause of the observed changes due to support and promoters can be ascribed to either changes in the energetics of the active sites or to the formation of new sites. In addition there is the possibility of synergistic effects resulting in the creation of new kinetic pathways either on the metal, on the interface, or on the support via spill-over effects. Such spill-over pathways have been deduced to exist for hydrogen sorbing on Rh/TiO_2 (*10, 11*).

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This paper reports a study, using frequency response chemisorption (FRC), of the kinetics of hydrogen chemisorption on Rh/TiO$_2$ catalysts, and the effect of alkali metal promotion on the nature of the H$_2$-sorbing sites. FRC allows for the identification of kinetically distinct adsorption pathways on the catalyst and we have previously reported on the existence of multiple distinct sites on both Rh and Ni on several supports. We report here on the effect of promoters on existing site occupancy and assess the possibility of the creation of new H$_2$-sorbing sites when promoters are introduced. We find considerable influence of the presence and nature of the alkali metal on the relative populations and apparent kinetic parameters. A comparison of reported CO and olefin hydrogenation rates with the predominance of sites found by FRC, suggests relationships between specific hydrogen sorbing sites and reaction pathways in these catalysts.

BACKGROUND

The technique of frequency response chemisorption consists of measuring the phase difference between an induced sinousoidal modulation in the volume of a closed adsorbent–adsorbate system and the resulting pressure modulation (*12–15*). For each process, characterized by a given set of adsorption and desorption rate constants, k_a and k_d, the phase difference maximum will occur at a modulation frequency which will be dependent on the pressure, temperature, site density, and amplitude of the volume modulation. Thus, the technique allows for the study of adsorption–desorption phenomena of individual sites, even though the processes are occurring simultaneously.

If the induced volume perturbation is small, the kinetic events can be approximated as first order processes. Yasuda showed that such a system could be represented by a real and an imaginary response functions, RRF and IRF, respectively:

$$\mathrm{RRF}(T,P,\omega) = v/p \cos\varphi - 1 = \sum \frac{\alpha_j\beta_j}{\beta_j^2+\omega^2} \quad (1)$$

$$\mathrm{IRF}(T,P,\omega) = v/p \sin\varphi = \sum \frac{\alpha_j\omega}{\beta_j^2+\omega^2} \quad (2)$$

where v and p are the volume and pressure amplitudes, ω is the modulation frequency, φ is the volume–pressure phase shift, and α_j and β_j represent partial derivatives of the rate equation for adsorption on site j (*13*).

Equation (2) has been described as the "adsorption-rate spectrum equation" because, at $\omega = \beta_j$, it exhibits maxima with a full width at half height equal to $2\beta_j\sqrt{3}$, regardless of the other parameters. Thus, its measurement can provide both a phenomenological fingerprint of the system as well as detailed quantitative information on the number and extent of the various adsorbing sites through proper deconvolution of the total signal.

The pressure dependence of the measured parameters α_j and β_j can be used to infer the mechanism of adsorption, as well as to obtain quantitative information on the adsorption and desorption rate constants and the site density of each individual site. For nondissociative Langmuir adsorption, the parameters α_j and β_j are given by

$$\beta_j = k_{aj}P + k_{dj}$$

and

$$1/\alpha_j = Y_j^2(P/k_{dj} + 1/k_{aj}) \quad (3)$$

whereas for a dissociatively adsorbed diatomic molecule, the relationships are

$$\beta_j = 2N_j\sqrt{k_{aj}k_{dj}P}$$

and

$$1/\sqrt{\alpha_j} = Y_j/N_j(\sqrt{P}/k_{dj} + 1/k_{aj}) \quad (4)$$

where N_j represent the number of sites of type j and $Y_j = \sqrt{V/(N_jRT)}$. Other adsorption models may be easily derived following previously developed formalism (*16*).

EXPERIMENTAL

Catalyst preparation and characterization. Supported Rh/TiO_2 catalysts were prepared by incipient wetness impregnation of titania (Degussa P-25) with an aqueous solution of rhodium chloride. The promoted catalysts were prepared in a similar manner using a single coimpregnation step of rhodium chloride and the appropriate alkali nitrate at a pH of 3.5. Metal loadings used were 0.6 and 3 wt% of Rh for the unpromoted catalysts and 3 wt% Rh and atomic ratio of 1/2 of alkali metal to rhodium for the promoted catalysts. A 1 wt% Rh/SiO_2 (Davison grade 59) was prepared using similar techniques. After impregnation the catalysts were dried overnight at 120°C and reduced *ex situ* in flowing H_2 at 400°C for 16 h then passivated in air at room temperature before further measurements.

The average Rh particle diameter was determined to be smaller than what could be measured using X-ray diffraction line-broadening techniques (*17*).

Static hydrogen chemisorption was determined using a conventional volumetric apparatus. The previously reduced samples were again reduced at 400°C, evacuated at 400°C for 1 h, and cooled to room temperature. Hydrogen was reintroduced to a pressure well above the saturation pressure, typically 200 Torr, and the catalysts were allowed to equilibrate for 36–48 h. The desorption isotherm was then measured by progressively reducing the hydrogen pressure and determining the equilibrium pressure after a 2-h interval. The reversible component of the chemisorption was determined by pumping on the catalyst for 12 min and measuring the amount of hydrogen readsorbed.

Previous work on the measurement of H_2 adsorption isotherms of these catalysts had shown that long adsorption periods were necessary for complete equilibration of the system and that when short adsorption periods were utilized, i.e., approximately 15–30 min after addition of hydrogen, much lower total hydrogen uptakes were recorded for the titania-supported catalysts (*16*). For this reason, only H_2 uptakes based on desorption isotherms were used in this work.

Frequency response chemisorption. The technique used in the FRC studies and the apparatus associated with this measurement have been previously described (*15*, *16*, *18*) and will not be extensively detailed here. Briefly, it consists of measuring the pressure amplitude of a sinusoidally modulated volume in a closed system containing an adsorbing gas and a catalyst. The absorption/desorption process produces a phase difference between the volume and pressure modulation and alters the expected pressure amplitude. By varying the frequency of modulation, the behavior of the phase differences and amplitudes can be recorded as functions of frequency and converted to the corresponding response functions using Eqs. (1) and (2). In the calculated imaginary response function—Eq. (2)—each maxima corresponds to one particular chemisorptive site or mode of chemisorption.

The procedure for obtaining the FRC spectrum of H_2 chemisorption on the various Rh catalysts was as follows. Approximately 3 g of the previously reduced and passivated catalysts were loaded into the FRC sample chamber. The sample was evacuated to ca. 10^{-6} Torr, and heated to 450°C under vacuum. Hydrogen was admitted into the sample compartment to a pressure of about 500 Torr, and the catalysts reduced statically for about 20 h. During reduction, the sample chamber was evacuated and refilled with hydrogen periodically in order to remove any water that may have formed during reduction. Following reduction the catalyst was evacuated to 10^{-6} Torr while hot and then cooled to 50°C. Hydrogen was then admitted and the sample allowed to equilibrate overnight prior to FRC measurements.

Measurements of the FRC spectrum were obtained between 10^{-2} and 10 rad/sec

TABLE 1

Summary of Catalysts Studied

Catalyst	Metal loading, %	Surface area, m^2/g	Crystallite[a] diam., Å	H$_2$ uptake, 10^{-6} mole/g	
				Total	Reversible
Rh/TiO$_2$	0.6	50	<40	18	—
Rh/TiO$_2$	3	50	<40	98	18
Rh–Li/TiO$_2$	3	50	<40	59	30
Rh–Cs/TiO$_2$	3	50	<40	21	6
Rh/SiO$_2$	1	300	<40	26	3

[a] By XRD.

using a series of four motor-drive combinations. Temperatures were controlled at 50 and 160°C. The measured $p(t)$ and $v(t)$ data were converted into the real and imaginary response signal using Eqs. (1) and (2).

A number of "blank" experiments were conducted in order to ascertain the absence of instrumental and/or diffusional artifacts in the observed signals, as described in detail previously (*16*). The results of these experiments indicated that the observed signal was in fact due to chemisorbed hydrogen.

RESULTS

The physical and adsorptive characteristics of the catalysts used in this study are shown in Table 1. In addition to the promoted and unpromoted Rh/TiO$_2$ catalysts, an unpromoted Rh/SiO$_2$ is also included for comparison. Silica has been demonstrated to exhibit little interactions with group VIII metals and as such serves as a "baseline" comparison in these studies.

The nature of the support or the Rh loading did not seem to have a significant effect on the hydrogen chemisorptive capacity of the catalysts, since all the unpromoted Rh catalysts showed approximately the same dispersion. Although titania has been reported to induce strong metal–support interactions (SMSI) and suppress hydrogen chemisorption when used as a support for group VIII metals, the long equilibration times used in this work allowed for filling of the slow chemisorptive sites (*9*). As has been reported in previous work, the similarity in the obtained values for Rh/TiO$_2$ and Rh/SiO$_2$, indicates that H$_2$ chemisorbing sites are still present in the titania "SMSI" catalysts, but they are not quite as kinetically accessible (*16, 18*).

Alkali metal promoted catalysts exhibited lower hydrogen uptake than the unpromoted counterparts. In the case of Rh–Li/TiO$_2$ it is not evident whether the reduced chemisorptive capacity is due to the presence of the alkali or simply to larger Rh crystallite size. However, in the case of Rh–Cs/TiO$_2$, the XRD results showed the metal crystallite to be smaller than could be accounted for based on the hydrogen uptake. Thus indicating that the alkali promoters indeed have suppressed the chemisorption capacity of the metal. Similar observations have been reported for Ru/SiO$_2$, Ru/TiO$_2$, and Ni/SiO$_2$ (*5, 19, 20*).

Frequency response chemisorption measurements were obtained at 48 and 160°C, at pressures ranging between 0.2 and 1.5 Torr. It is within these temperature and pressure ranges that optimum signal is observed in the FRC spectra. Typical FRC spectra taken at 50°C are shown in Fig. 1 for the 3% Rh/TiO$_2$ (promoted and unpromoted) and the 1% Rh/SiO$_2$ catalysts. The experimentally obtained data were deconvoluted by fitting one or more functions of

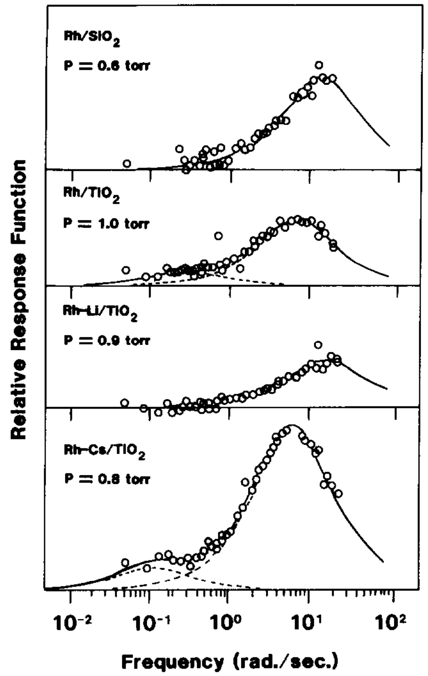

FIG. 1. Frequency response spectra for the chemisorption of H_2 on supported rhodium at 48°C.

the type given in Eq. (2), in order to obtain values of α and β for each component of the spectrum or "site." At 48°C only one site is prominent in all catalysts, and its position does not seem to be strongly dependent on either the type of support or the existence or promoters. In some cases, most notably Rh–Cs/TiO_2, a small second feature is observed at slower modulation frequencies, but its existence is not clear in other catalysts.

Typical FRC spectra obtained at 160°C for all the catalysts under study are shown in Fig. 2. In contrast with the relatively simple and similar low temperature results, the observed FRC signal in this case is highly dependent on support, promoter, and loading.

Deconvolution of the spectra shows that up to three sites are necessary to properly fit the experimental data. This is in contrast with our earlier communication in which, for unpromoted Rh/TiO_2, we reported the existence of only two high temperature sites (*16*). Improved experimental procedures now lead us to postulate the existence of at least three high temperature sites for promoted and unpromoted Rh/TiO_2 and at least two sites for Rh/SiO_2. Figure 3 shows a one-, two-, and three-peak fit of typical experimental data, which clearly shows that indeed three kinetically distinct sites for hydrogen chemisorption can be detected using FRC.

A summary of the derived response functions, α_j and β_j, for the various chemisorbing sites identified is given in Table 2. For convenience, the low temperature response functions have been subscripted 1 and 2, while the high temperature functions have been subscripted 3 to 5.

DISCUSSION

Since both support and alkali promoters can influence the activity and selectivity of

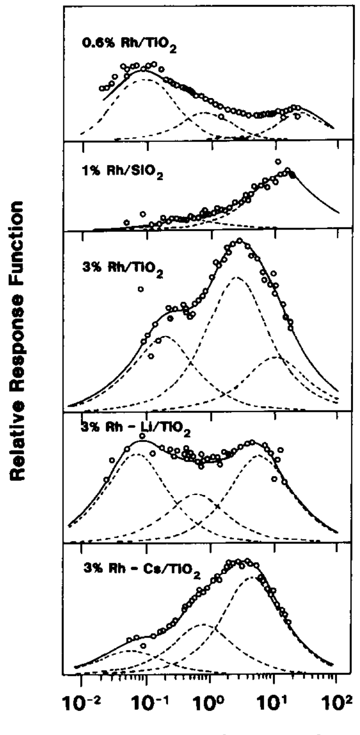

FIG. 2. Frequency response spectra for the chemisorption of H_2 on supported rhodium at 160°C and 0.5 Torr.

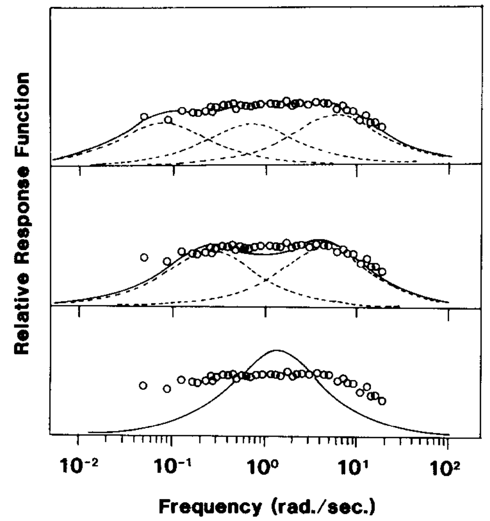

FIG. 3. Frequency response spectrum for the chemisorption of H_2 on 3% Rh/TiO$_2$ at 160°C and 0.9 Torr, showing one-, two-, and three-peak fit of the experimental data.

supported metal catalysts, it is not surprising to find that both support and promoters can also affect the kinetics of chemisorption of a probe sorbing molecule, such as hydrogen. At low temperature, however, only minor differences in the qualitative features of the FRC spectra are evident. It is difficult to consider these minor differences to be significant, since they may simply reflect small variations between catalyst preparation or pretreatment.

Analysis of the pressure dependence of the response functions for the unpromoted Rh catalysts at low temperature has shown a linear dependence between β_1 and pressure, as predicted by Eq. (3) for *nondissociative Langmuir kinetics* (*16, 18*). This conclusion can now be extended to the promoted catalysts, where a similar dependence is observed. Thus, in all cases studied, a significant amount of hydrogen is sorbing, at low temperatures, in a mode which behaves as expected for a nondissociative state. This state could either correspond to a true molecular adsorption, a weakly bound precursor to dissociatively adsorbed H_2, or even a dissociatively adsorbed H_2 on an ensemble of metal atoms. FRC techniques can not distinguish between these possibilities. Regardless, the amount sorbing in this state can be estimated from the pressure dependence of the FRC spectra and is typically in the range of 3 to 8 μmol/g, only a small fraction of the total chemisorption and about the same amount as the observed reversible chemisorption. Thus, it is likely that this "molecular" state is associated with the reversibly chemisorbed state.

The observation of this "molecular" state is noteworthy, since most studies consider H_2 to only adsorb in a dissociative state. There is previous strong evidence, however, for the existence of molecularly

TABLE 2

Summary of FRC Parameters for Supported Rhodium Catalysts

Catalyst	Temp., °C	Pressure, Torr	Response functions									
			α_1	β_1	α_2	β_2	α_3	β_3	α_4	β_4	α_5	β_5
Rh/SiO$_2$	48	0.6	4.8	13.9	—	—	—	—	—	—	—	—
Rh/TiO$_2$	48	1.0	1.8	7.1	0.014	0.29	—	—	—	—	—	—
Rh–Li/TiO$_2$	48	0.9	2.2	14.1	—	—	—	—	—	—	—	—
Rh–Cs/TiO$_2$	48	0.8	3.0	5.3	0.008	0.10	—	—	—	—	—	—
Rh/SiO$_2$	160	0.5	—	—	—	—	3.45	13.7	0.02	0.52	—	—
Rh/TiO$_2$	160	0.4	—	—	—	—	2.65	10.7	1.74	2.7	0.065	0.19
Rh–Li/TiO$_2$	160	0.4	—	—	—	—	2.25	5.7	1.26	0.58	0.014	0.07
Rh–Cs/TiO$_2$	160	0.5	—	—	—	—	2.20	4.8	1.90	0.80	0.006	0.06

TABLE 3

Kinetic Parameters for H_2 Chemisorption on Rh/TiO_2

Catalyst	Site 5			Site 4			Site 3		
	k_a[a]	k_d[b]	N[c]	k_a[a]	k_d[b]	N[c]	k_a[a]	k_d[b]	N[c]
Rh/TiO_2	—	—	—	1×10^6	2×10^5	4	2×10^5	2×10^6	2
$Rh–Li/TiO_2$	7×10^4	3×10^3	4	6×10^5	1×10^3	3	6×10^5	1×10^6	2
$Rh–Cs/TiO_2$	—	—	—	—	—	—	1×10^6	3×10^6	1

[a] $Torr^{-1}\ sec^{-1}$.
[b] sec^{-1}.
[c] Micromoles/g cat.

adsorbed hydrogen on rhodium catalysts (*21*), and some investigators have attributed methanol synthesis to the addition of molecular H_2 to CO (*22*). It is interesting to note that this molecular hydrogen state exists on all the catalysts and that its kinetic parameters are not very sensitive to either support or promoter. Its existence, however, may not pose any relation to the catalytic properties of the material since this state is only evident at low temperatures (i.e., ambient) and it is likely that at reaction temperature the state is not significantly populated.

At high temperature, the influence of the support is clearly reflected on the chemisorption kinetics of hydrogen. Whereas Rh/SiO_2 exhibits only one major FRC site, when titania is used as support a total of three major sites are observed. Of the three sites observed in the 3% Rh/TiO_2 catalyst, *site 3* corresponds in both amplitude and frequency to the major Rh/SiO_2 site and, based on its kinetic parameters, may therefore be assigned to *hydrogen sorbing on Rh metal sites*. Thus, the additional two new sites (sites 4 and 5) must be due to the influence of the support on the metal and are perhaps due to the SMSI nature of titania supported catalysts.

The addition of alkali promoters seem to have an effect on the kinetic parameters of site 3, resulting in a slight shift of the signal maximum to lower frequencies. This shift can be envisioned as due to an increase in the binding energy of the hydrogen on this site resulting in a slower adsorption–desorption process from the surface, hence lower frequencies. In addition to the frequency shift, a large effect is evident on the relative amplitudes of sites 3, 4, and 5 upon alkali metal addition. Addition of Li to Rh/TiO_2 results in a reduction of chemisorption on site 4, but leaves sites 3 and 5 largely unaffected. In contrast, the addition of Cs as a promoter affects the chemisorption of both sites 4 and 5.

Measurements of the pressure dependence of the response functions of the high temperature sites show that the hydrogen chemisorption of these three sites behave according to *dissociative Langmuir kinetics*. Experimental limitations, however, prevented the determination of accurate values for the number of sites corresponding to each process and only an estimate of the corresponding kinetic parameters were obtained. These are shown in Table 3.

Further insight into the nature of sites 4 and 5 can be gained by comparing the FRC spectra of the two Rh/TiO_2 catalysts with markedly different metal loadings. The slowest site (site 5) is virtually unchanged in both position and magnitude, but sites 3 and 4 are smaller in the low loading catalyst. One possible interpretation is that site 5 corresponds to hydrogen from the support, thus it remains constant regardless of the metal loading. Although FRC experiments on pure titania showed that hydrogen does not sorb under these conditions, the mechanism of "spill-over" can still account for the presence of hydrogen on the support.

Other studies have shown the existence of multiple chemisorbing sites on Rh catalysts, and some have even suggested the existence of spill-over hydrogen on the support, which can desorb at high temperature (*10, 11, 23*). Temperature programmed desorption (TPD) studies of Rh/SiO_2 and Rh/TiO_2 have shown evidence for one low temperature and one high temperature site in the former and at least three sites in the latter (*24, 25*). Other recent TPD studies on alkali promoted supported rhodium corroborates our observations of multiple high temperature sites and shifts in binding energies with promotion (*26*).

Work on the effect of alkali promotion on the CO hydrogenation reaction over supported Rh have shown activities and selectivities to be highly dependent on the support and promoter. Comparison of various alkali-promoted Rh/TiO_2 show the rate of CO conversion to be highly dependent on the promoter used, and to increase in the order: none $>$ Li $>$ K $>$ Cs (*6*). Interestingly, the total amplitude of the various components of the FRC spectra follow the same order. The addition of small amounts of ethylene as a probe molecule to the CO hydrogenation reaction has shown that Rh/TiO_2 catalysts have much higher hydrogenation activity than Rh/SiO_2 and that this hydrogenation activity is reduced when alkali promoters are used, particularly in the case of cesium (*27*). These observations also agree with our observed FRC results where much higher total signal amplitude is observed for Rh/TiO_2 than for Rh/SiO_2 and the amplitude is diminished by addition of promoters. Cesium in particular was noted to suppress site 5, which is presumed to correspond to hydrogen spill-over. If indeed site 5 is due to hydrogen spill-over, it would not be expected to have much catalytic activity for a metal-based reaction, but it could still act as a hydrogen supply and thus enhance hydrogenating activity.

The nature of site 4 is still not clear. Comparison of the FRC results between Rh/SiO_2 and Rh/TiO_2 indicate that this site is support-dependent, but not a support site. One possibility is that site 4 corresponds to the rhodium–titania interface or to specific rhodium ensembles which are induced during high temperature reduction in the presence of titania. Regardless, it is evident that alkali promotion can easily suppress this type of site, perhaps via complex formation or acid–base reactions. This type 4 site is presumably also active for CO hydrogenation as evidenced by reported decreases in activity upon Li-promotion of Rh/TiO_2 (*27*).

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