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NOTE

Impact of Readsorption Effects and Their Removal from Surface Reaction Parameters Obtained by Isotopic Transient Kinetic Analysis: Methanol Synthesis on Pd/SiO_2

Steady-state isotopic transient kinetic analysis (SSITKA) technique is a powerful tool in the field of heterogeneous catalysis for the study of surface reactions. SSITKA was developed in large part by Biloen (1), Bennett (2), Happel (3), and Bell (4). SSITKA can be used to evaluate coverages of intermediates, their activities, site heterogeneity, and surface reaction mechanisms (5–11). This technique has been recently reviewed in detail (7). The application of SSITKA to the study of reactions on catalyst surfaces permits us to develop a better understanding of reaction at the site level. However, such an application can be complicated by the presence of readsorption of the products (7, 12, 13). Readsorption causes an overestimation of the average surface residence time on the active sites and of the concentration of active intermediates.

Pd is one of the most active catalysts for MeOH synthesis from CO and H_2, probably because of its weak ability to dissociate CO and its moderate ability to activate H_2 (14–18). Pd/SiO_2, especially, catalyzes the formation of MeOH with a high selectivity with no detectible amounts of dimethyl ether (DME) formation (19–21). MeOH can readsorb easily on both active (Pd) and inactive (Pd and support) sites.

The purpose of this study was to evaluate the effect of readsorption of product MeOH on the surface reaction parameters obtained by SSITKA for Pd/SiO_2 and to find means by which this effect (readsorption) could be removed for this and potentially other reactions. Such removal would result in better estimations of site activities and concentrations of active sites.

The surface area and the pore volume of the SiO_2 support used (Davison 952), obtained by nitrogen physisorption at 77 K, were found to be 219 m^2/g and 0.51 cm^3/g. The impurities in the SiO_2 were determined by inductively coupled plasma (ICP) to be Mg (150 ppm), Na (570 ppm), Ca (750 ppm), Ti (120 ppm), Al (220 ppm), Fe (96 ppm), P (83 ppm), K (160 ppm), and S (30 ppm). A 5 wt% Pd/SiO_2 catalyst was prepared by the incipient wetness technique using an aqueous solution of $PdCl_2$ (Aldrich). The dried catalyst was calcined in flowing air at 400°C and reduced in flowing H_2 at 400°C for 5 h following a 1°C/min ramp. Additional details about the preparation procedure can be found in Ref. (12). The amount of Cl remaining in the catalyst after calcination and reduction was not determined.

CO chemisorption measurements were carried out according to the method used by Kazi *et al.* (22) using 1 g reduced/passivated Pd/SiO_2 catalyst which was rereduced in H_2 and desorbed at 400°C prior to the chemisorption measurements. The isotherm of reversibly adsorbed CO was determined after that for total CO after evacuation for 20 min at room temperature. CO_{irrev} was determined from the difference in the extrapolated total and reversible isotherms at zero pressure ($CO_{tot} - CO_{rev}$). The number of Pd metal atoms at the surface was determined using the relationship $CO_{irrev}/Pd_s = 1$. The dispersion of the Pd particles was found to be 17% with a maximum experimental error of ±0.9%. The average particle size of the Pd crystallites (d_p) was calculated to be 5.5 nm. Additional details about this procedure are given in references (12, 22).

A micro, fixed-bed reactor was used for studying MeOH synthesis, and differential reaction conditions were employed to minimize mass and heat transfer limitations. A flow of 60 cm^3/min of H_2 (Praxair, 99.999% pure) was used to rereduce the Pd/SiO_2 catalyst by ramping the temperature by 1°C/min to 400°C and holding for 5 h. After completing the rereduction, the reaction was started at 220°C and 1.8 atm by setting the total flow of H_2 (Praxair, 99.999% pure) and CO (Praxair, 99.999% pure) to be equal to 36 cm^3/min (STP), with $H_2/CO = 8$. After reaching steady-state reaction, the total flow rate of the reactant stream was varied between 45 and 18 cm^3/min (STP) with gas chromatography analysis of the product stream in order to determine the effect of interparticle readsorption. At steady state, the reaction temperature was varied between 220 and 190°C in order to obtain an Arrhenius plot for the determination of the apparent activation energy of reaction (E_{app}). Isotopic transient measurements were taken by switching from ^{12}CO to ^{13}CO at steady state at each flow rate of the reactants. A Leybold-Inficon Auditor-2 mass spectrometer with a high-speed data acquisition system was used to detect the amounts of the different isotopically labeled species. The switching between ^{12}CO and ^{13}CO was done without affecting the stability of the reaction. Ar was used as a

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tracer in the ^{12}CO flow to account for the gas phase holdup. The concentration of Ar (5% of the ^{12}CO stream) was not sufficient to perturb the reaction stationary state during the switch from $^{12}CO + Ar$ to ^{13}CO. Additional details about the reaction and SSITKA procedures are given in Ref. (12).

The impact of P_{MeOH} on the SSITKA parameters obtained during MeOH synthesis on Pd/SiO$_2$ was also investigated. After establishing steady-state reaction at 220°C with P_{H_2} and P_{CO} of 1.6 and 0.2 atm, respectively, and a total flow rate of 36 cm^3/min, steady-state was reestablished at 220°C with P_{H_2}, P_{CO}, and P_{He} of 1.6, 0.2, and 0.2 atm, respectively. Then, reaction was carried out at these same partial pressures of H_2 and CO but replacing He with He containing 2000 ppm of $^{12}CH_3OH$. These experiments were performed at various flow rates of the reactant mixture of CO, H_2, and He (or He containing 2000 ppm of $^{12}CH_3OH$) ranging between 20 and 50 cm^3/min. The amount of MeOH-containing He added was varied in order to vary P_{MeOH}.

Table 1 presents the results of CO hydrogenation on Pd/SiO$_2$ at 220°C and 1.8 atm for different reactant flow rates after 10 h reaction, corresponding to steady-state reaction conditions. The highest CO conversion under the conditions used was less than 1%, allowing differential reaction conditions to be assumed. No mass or heat transfer limitations were detected for any of the reaction experiments as evidenced by appropriate apparent activation energies for the formation of MeOH. The apparent activation energy of MeOH formation for Pd/SiO$_2$ at steady state for both the highest and the lowest flow rates was equal to 62 ± 4 kJ/mol, similar to values reported in the literature for supported Pd catalysts (13, 23). The conversions of CO to MeOH for the various conditions studied were much smaller than those for equilibrium (less than 10% of the equilibrium value). Thus, based on this fact and the appropriateness of the apparent activation energy of MeOH, it can be concluded that MeOH synthesis was limited by reaction kinetics and not by thermodynamics. The H_2/CO ratios used were high enough ($H_2/CO = 8$) to minimize deactivation at steady state. The selectivity for MeOH formation for Pd/SiO$_2$ was 98% for all the different flow rates used, and no DME formation due to secondary reaction of MeOH was detected.

From Table 1 it is clear that, by increasing the flow rate of the reactant stream, the conversion percentage of CO to products decreased (as to be expected). In addition, there was a small real increase in the total rate of reaction due to the negative dependence of the rate of formation of MeOH on P_{MeOH}. In another paper (12), it was shown that, under the reaction conditions utilized here, the power law rate expression for MeOH formation (at low CO conversion) for this catalyst is given by

$$\mathrm{Rate}_{MeOH} = kP_{H_2}^{+1.16}P_{CO}^{+0.16}P_{MeOH}^{-0.15}.$$

The time-on-stream behavior of the rate of formation of MeOH over Pd/SiO$_2$ (Fig. 1) included an initial induction period in the rate of formation of MeOH prior to reaching steady-state reaction. The time of the induction period was ≤30 min. This induction phenomenon is explored in detail elsewhere (12).

SSITKA was used to determine the average surface residence times (τ_{MeOH}) and concentrations (N_{MeOH}) of the active MeOH intermediates. Figure 2 shows a typical set of normalized isotopic transients for MeOH ($^{12}CH_3OH$) and Ar obtained by switching between a stream containing ^{12}CO and Ar and another stream containing ^{13}CO at steady state at 220°C (reactant flow rate of 36 cm^3/min, and partial pressures of H_2 and CO of 1.6 and 0.2 atm, respectively). The average surface residence time for the intermediates leading to MeOH (τ_{MeOH}) is equal to the area between the normalized transients of MeOH and Ar [see Ref. (7) for a review of this determination]. Table 1 shows the results for

TABLE 1

Reaction and SSITKA Results for MeOH Synthesis on 50 mg of Pd/SiO$_2$[a]

Total reactant flow rate (cm^3/min)	CO conversion (%)	Total rate of CO conversion[b] (μmol/s/g of Pd/SiO$_2$)	CH$_4$ selectivity (%)	MeOH selectivity (%)	P_{MeOH} in effluent (Pa)	τ_{MeOH}[c] (sec)	N_{MeOH}[d] (μmol/g of Pd/SiO$_2$)
18	0.25	0.069	2	98	50	158	10.7
27	0.18	0.073	2	98	35	140	10.0
36	0.14	0.075	2	98	27	126	9.2
45	0.12	0.079	2	98	23	116	9.0

[a] For steady-state reaction (after 10 h) at 220°C, 1.8 atm, and $H_2/CO = 8$.

[b] Maximum error = ±5%.

[c] Average surface residence time (τ_{MeOH}) of the active MeOH intermediates, maximum error = ±3 sec.

[d] N_{MeOH} = average surface concentration of the active MeOH intermediates = $R_{MeOH} * \tau_{MeOH} = R_{CO} * [S_{MeOH}/100] * \tau_{MeOH}$.

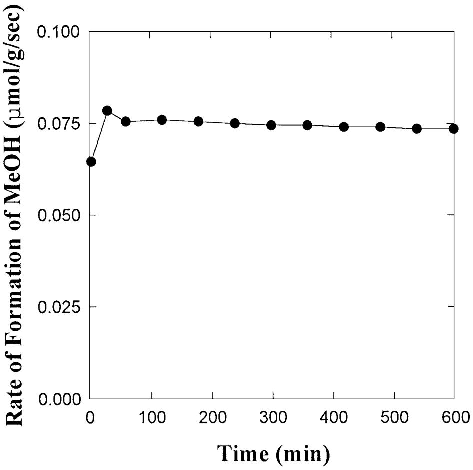

FIG. 1. Rate of formation of MeOH on Pd/SiO$_2$ vs time-on-stream during CO hydrogenation (at 220°C, 1.8 atm, and total reactant flow rate of 36 cm^3/min).

τ_{MeOH} under steady-state conditions for the various flow rates used.

One of the main parameters from SSITKA is the surface concentration of intermediates (N_i), obtained by multiplying the rate of formation of a product by its average surface residence time (7). For Pd/SiO$_2$, N_{MeOH} represents the number of MeOH intermediates at any time, including molecules on active Pd sites as well as readsorbed on inactive Pd and/or SiO$_2$ sites. Table 1 contains the values of N_{MeOH} determined for Pd/SiO$_2$ at various flow rates.

Due to the fact that MeOH can readsorb on active, less active, and/or possibly inactive reaction sites (12, 13), changing the flow rate during CO hydrogenation is able to modify this phenomenon by affecting the residence time of product MeOH in the catalyst bed. Depending on its extent, readsorption can have a significant effect on the value of τ_{MeOH} obtained, as reported elsewhere (12, 13). By plotting τ_{MeOH} versus space time [residence time in the catalyst bed] (Fig. 3), it is clear that τ_{MeOH} increased with an increase in space time. This increase in the value of τ_{MeOH} with an increase in the space time was significant (ca. 25% upon doubling the space time). By extrapolating τ_{MeOH} to space time = 0, a more accurate estimation of MeOH surface residence time due to reaction (τ^0_{MeOH}) can be determined. From Fig. 3, τ^0_{MeOH} was found to be ca. 91 sec. This procedure acts to eliminate interparticle readsorption; however, τ^0_{MeOH} is still an overestimation of τ_{reaction} due to possible readsorption within the pores where primary reaction occurred.

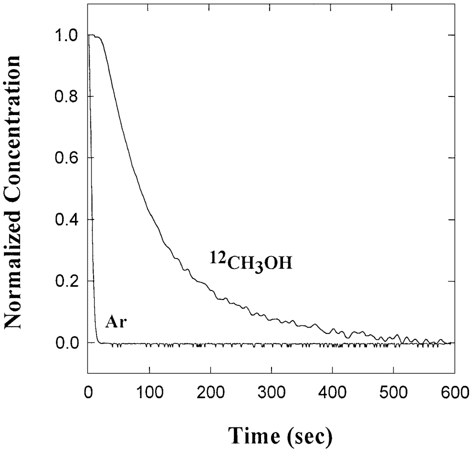

FIG. 2. Typical isotopic transients of ^{12}CH$_3$OH and Ar at steady state during MeOH synthesis on Pd/SiO$_2$.

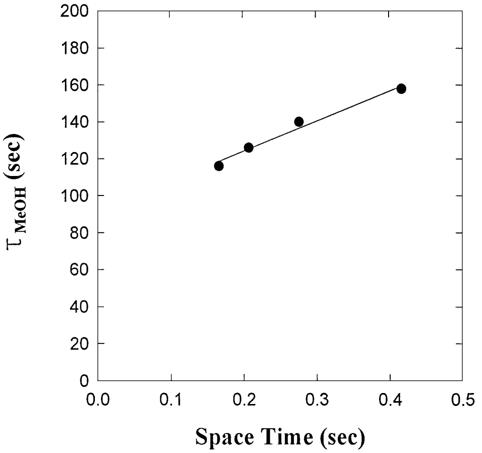

FIG. 3. τ_{MeOH} vs space time during steady-state MeOH synthesis at 220°C (used to determine τ^0_{MeOH}).

Because of variations in the value of P_{MeOH} for different reactant flow rates, the value of τ^0_{MeOH} determined from Fig. 3 does not account for any impact that P_{MeOH} may have had. Nwalor *et al.* (24) found that during methanation on Ni, by adding H$_2$O in order to increase $P_{\text{H}_2\text{O}}$, $\tau_{\text{H}_2\text{O}}$ for labeled H$_2$O being formed decreased due to the increase in competition for H$_2$O adsorption sites. Hence, by performing MeOH synthesis over Pd/SiO$_2$ while simultaneously adding small amounts of unlabeled MeOH to the reactant feed stream, the relationship between τ_{MeOH} and P_{MeOH} can be established. Table 2 contains such results and indicates that a relationship exists between τ_{MeOH} and the total P_{MeOH}. By plotting τ_{MeOH} versus the average partial pressure of MeOH in the catalyst bed, $P_{\text{MeOH,avg.}}$, where

$$P_{\text{MeOH,avg.}} = P_{\text{MeOH,added}} + (1/2)P_{\text{MeOH,reaction}},$$

the significance of the effect of P_{MeOH} on this SSITKA parameter can be easily seen. Figure 4 indicates that the competition between MeOH species (formed vs added) for readsorption on available sites present on the Pd/SiO$_2$ catalyst increased significantly with increasing P_{MeOH}, resulting in a decrease in the average value of τ_{MeOH} determined

TABLE 2

Reaction and SSITKA Results for MeOH Synthesis on 50 mg of Pd/SiO$_2$ during Addition of MeOH[a]

F_{H_2}[b] (cm^3/min)	F_{CO}[c] (cm^3/min)	F_{He}[d] (cm^3/min)	$F_{He+MeOH}$[e] (cm^3/min)	CO conversion (%)	Total rate of CO conversion[f] (μmol/s/g of Pd/SiO$_2$)	P_{MeOH} formed (Pa)	P_{MeOH} added (Pa)	τ_{MeOH}[g] (sec)
40	5	5	0	0.12	0.082	24	0	111
40	5	0	5	0.11	0.073	21	40	94
40	5	0	4	0.11	0.076	23	32	96
40	5	0	3	0.11	0.076	23	24	99
32	4	4	0	0.15	0.080	30	0	121
32	4	0	4	0.13	0.072	27	40	99
32	4	0	3	0.14	0.074	27	30	101
32	4	0	2	0.14	0.076	28	20	104
24	3	3	0	0.19	0.078	39	0	135
24	3	0	3	0.18	0.073	36	40	106
24	3	0	2	0.18	0.074	37	27	109
24	3	0	1	0.19	0.076	38	14	120
16	2	2	0	0.26	0.072	53	0	153
16	2	0	2	0.25	0.068	51	40	120
16	2	0	1.5	0.25	0.069	51	30	128
16	2	0	1	0.25	0.069	51	20	129

[a] For steady-state reaction (after 10 h) at 220°C, keeping P_{H_2} and P_{CO} constant with values of 1.6 and 0.2 atm, respectively. MeOH selectivity was equal to 98% under all conditions used.

[b] H$_2$ flow rate.

[c] CO flow rate.

[d] He flow rate.

[e] Flow rate of He containing 2000 ppm MeOH.

[f] Maximum error = ±5%.

[g] Maximum error = ±3 sec.

for the labeled MeOH being synthesized. The addition of MeOH aids in addressing the issue of readsorption within both the catalyst bed and the pores. Figure 4 indicates that τ_{MeOH} approaches asymptotically a minimum value as P_{MeOH} increases.

By plotting values of τ_{MeOH} from Fig. 4 at fixed P_{MeOH} (Fig. 5), it is clear that there is still a linear dependency of τ_{MeOH} on space time even holding P_{MeOH} constant; however, this dependency appears to have a slightly greater slope than the one where P_{MeOH} was not constant (Fig. 3).

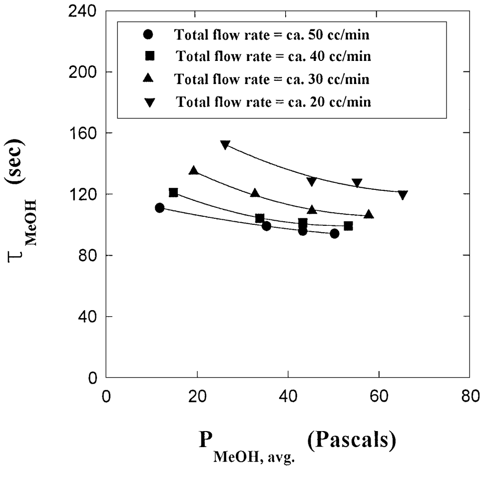

FIG. 4. τ_{MeOH} vs average P_{MeOH} at various flow rates during steady-state MeOH synthesis at 220°C.

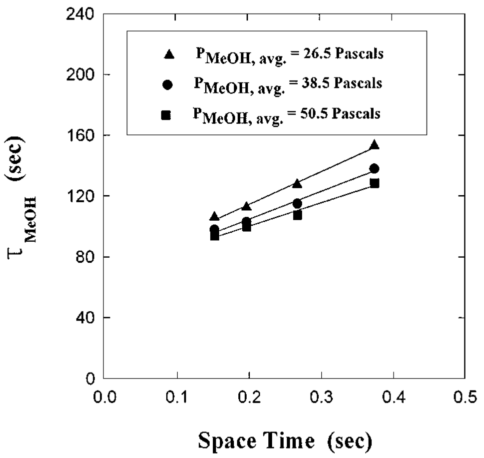

FIG. 5. τ_{MeOH} vs space time at constant average P_{MeOH} during steady-state MeOH synthesis at 220°C (used to determine τ^{00}_{MeOH}).

Extrapolation of the data in Fig. 4 to zero space time should result in a value for τ_{MeOH}, $\tau^{00}_{\mathrm{MeOH}}$, corrected for both interparticle and intrapore readsorption. $\tau^{00}_{\mathrm{MeOH}}$ (ca. 70 sec) can be easily seen to be less than 91 sec (τ^{0}_{MeOH}), the value calculated after removal of only the interparticle readsorption. Thus, a more exact pseudo-first-order intrinsic activity, k_{i}, of the sites producing MeOH can be evaluated using $\tau^{00}_{\mathrm{MeOH}}$, where $k_{\mathrm{i}} = 1/\tau^{00}_{\mathrm{MeOH}}$. The intercepts of all the plotted lines in Fig. 5 are almost the same (70 ± 2 sec), which suggests that $\tau^{00}_{\mathrm{MeOH}}$ does not vary significantly depending on the value of $P_{\mathrm{MeOH,avg.}}$ fixed.

The impact of readsorption of MeOH is less important on N_{MeOH} because, as mentioned earlier, N_{MeOH} represents the total number of MeOH surface intermediates at any time including molecules adsorbed on different sites. However, in order to evaluate the exact number of active Pd sites producing MeOH at any given time (N^{00}_{MeOH}), one can use the estimated value of τ_{MeOH} of reaction ($\tau^{00}_{\mathrm{MeOH}}$) with the equation

$$N^{00}_{\mathrm{MeOH}} = R_{\mathrm{MeOH}} * \tau^{00}_{\mathrm{MeOH}}.$$

Thus, for the conditions utilized in this investigation, the concentration of active Pd sites producing MeOH at any given time is estimated to be 5.2 ± 0.2 μmol/g of catalyst. This is equivalent to $\Theta_{\mathrm{Pd}} = 0.065 \pm 0.003$, assuming 1 MeOH intermediate per active surface Pd atom. The other surface Pd sites are vacant, occupied by readsorbed MeOH (ca. 5 μmol/g of catalyst for the reaction conditions used in this study), occupied by CO which does not react to MeOH, or deactivated.

One final point that should be addressed is the possible impact on the SSITKA parameters of the reversible reaction ($\mathrm{MeOH} \rightarrow \mathrm{CO} + \mathrm{H_2}$) which can occur on the active Pd sites. Only carbon exiting the reactor as MeOH was included in the determinations. Carbon which went through the reversible reaction ($\mathrm{CO} \rightarrow \mathrm{MeOH} \rightarrow \mathrm{CO}$) exited the reactor as CO and was not counted. For reaction in a differential bed reactor at relatively high flow rates where readsorption is limited, the number of molecules undergoing double reversible reaction ($\mathrm{CO} \rightarrow \mathrm{MeOH} \rightarrow \mathrm{CO} \rightarrow \mathrm{MeOH}$) is insignificant. Thus, for this study, reaction reversibility did not have a negative impact on the surface reaction parameters determined or calculated. However, the impact of reversibility undoubtedly would become more problematic at equilibrium conversion to MeOH and a low space velocity.

Means by which readsorption effects can be removed from SSITKA-determined surface reaction parameters were investigated for MeOH synthesis on $\mathrm{Pd/SiO_2}$ at 220°C. It was found that the average surface residence time of intermediates leading to MeOH (τ_{MeOH}) could be corrected for interparticle readsorption of MeOH (τ^{0}_{MeOH}) by extrapolation to zero space time (zero residence time in the catalyst bed). However, in order to account for both interparticle and intrapore readsorption of MeOH, τ_{MeOH} had to be extrapolated to zero space time holding P_{MeOH} constant ($\tau^{00}_{\mathrm{MeOH}}$). The results obtained in this investigation under the conditions utilized suggest that the value determined for $\tau^{00}_{\mathrm{MeOH}}$ is independent of the P_{MeOH} used. This corrected value of $\tau_{\mathrm{MeOH}}(\tau^{00}_{\mathrm{MeOH}})$ should be equal to the actual average surface residence time on the active Pd sites of carbon in the reaction intermediates forming MeOH. Without this correction for MeOH, the value determined for τ_{MeOH} was as much as double the corrected value of 70 sec at the highest space times, even though a differential reactor was used.

The exact value of the pseudo-first-order intrinsic activity of the sites producing MeOH is best estimated from the reciprocal of $\tau^{00}_{\mathrm{MeOH}}$, $k_{\mathrm{i}} = 1/\tau^{00}_{\mathrm{MeOH}}$. At 220°C and under the conditions used, k_{i} of the Pd was determined to be $14.3 \times 10^{-3}\ \mathrm{sec}^{-1}$. An estimation of the exact number of active Pd sites producing MeOH at any time under the reaction conditions utilized in this study was made using the corrected value of $\tau_{\mathrm{MeOH}}(\tau^{00}_{\mathrm{MeOH}})$ and was equal to 5.2 μmol/g of catalyst, equivalent to $\Theta_{\mathrm{Pd}} = 0.065$.

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