JOURNAL OF CATALYSIS **171,** 333–338 (1997)
ARTICLE NO. CA971797

NOTE

Analysis of Sequential Reactions in Bifunctional Catalyst Systems Using Isotopic Transient Kinetics: Methanol Synthesis on $Pd/SiO_2 + Al_2O_3$

Pd is one of 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 (1–5). Pd/SiO_2, especially, catalyzes the formation of MeOH with a high selectivity with no detectible dimethyl ether (DME) formation (6–8). Pd catalysts prepared using acidic supports (such as HY, Al_2O_3, and SiO_2–Al_2O_3), on the other hand, have been found to result in the production of DME during MeOH synthesis (9, 10). This DME formation has been concluded to occur by the dehydration of MeOH on acid sites on the support (11, 12). Hence, the formation of DME over Pd supported on acidic supports proceeds through a sequential reaction—the formation of MeOH from the reaction of CO and H_2 on the active Pd surface, followed by the dehydration of MeOH forming DME and H_2O on acid sites of the support.

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 (13), Bennett (14), Happel (15), and Winslow and Bell (16). SSITKA can be used to evaluate coverages of intermediates, their activities, site heterogeneity, and surface reaction mechanisms (17–23). This technique has been recently reviewed in detail (19).

The application of SSITKA to the study of MeOH synthesis over Pd on a wide variety of supports offers an opportunity to develop a better understanding of the influence of the support on the reaction characteristics. However, such an application can be complicated by secondary reaction of MeOH on acidic sites which may be present on the support. SSITKA has not been previously effectively applied to the study of sequential reactions in a catalytic system where readsorption is significant. Thus, the purposes of this study were (a) the development of isotopic transient analysis of such reactions and (b) the investigation by SSITKA of MeOH synthesis in a multisite environment. Physical mixtures of Pd/SiO_2 and γ-Al_2O_3 were used in this study to provide bifunctionality in order to keep the characteristics of the Pd sites constant. By using different catalyst configurations, reaction and readsorption of the MeOH and DME on the metal and acid sites were able to be analyzed.

The surface areas and the pore volumes of the SiO_2 support used (Davison 952) and of γ-Al_2O_3 (Vista B), obtained by nitrogen physisorption at 77 K, were found to be as follows: SiO_2, 219 m^2/g and 0.51 cc/g; γ-Al_2O_3, 299 m^2/g and 1.69 cc/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). The γ-Al_2O_3 had the following impurities: Mg (5 ppm), Na (300 ppm), Ti (5 ppm), and Fe (50 ppm).

Palladium chloride (Aldrich) was used to prepare a 5 wt% Pd/SiO_2 catalyst by the incipient wetness technique using an aqueous solution. After the impregnation step, the dried catalyst was then calcined in flowing air and reduced in flowing H_2 at 400°C. Additional details about the preparation procedure can be found in Ref. (25).

CO chemisorption measurements were carried out according to the method used by Kazi *et al.* (24) using 1 g of reduced Pd/SiO_2 catalyst. Specific details about this procedure are given in that reference. The number of Pd metal atoms at the surface was determined using the relationship $CO_{irrev}/Pd_s = 1$, where $CO_{irrev} = CO_{tot} – CO_{rev}$. 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 characterization can be found in Ref. (25).

A micro, fixed-bed reactor was used for studying this reaction, and differential reaction conditions were employed to minimize mass and heat transfer limitations. Different catalyst configurations were employed in this investigation: 50 mg of Pd/SiO_2; physical mixtures of 50 mg Pd/SiO_2 with either 50 mg of SiO_2, 50 mg of γ-Al_2O_3, or 100 mg of γ-Al_2O_3; a dual bed consisting of a physical mixture of 50 mg Pd/SiO_2 and 50 mg Al_2O_3 followed by 50 mg of SiO_2. After completing rereduction of the Pd at 400°C, 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 cc/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 cc/min (STP) with GC analysis of the product stream in order to determine the effect of interparticle readsorption. Isotopic transient measurements were taken by switching from ^{12}CO (Praxair, 99.999% pure) to ^{13}CO (Isotech, 99.999% pure)

0021-9517/97 $25.00

at steady state at each flow rate of the reactants. The switching between ^{12}CO and ^{13}CO was done without affecting the stability of the reaction. Ar was used as a 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 reference (25).

The reaction of DME on both Pd/SiO_2 and γ-Al_2O_3 at the reaction conditions utilized was determined. After pretreating 50 mg of Pd/SiO_2 or γ-Al_2O_3 with H_2 at 400°C, the reaction was carried out at 220°C and 1.8 atm using the same fixed-bed microreactor and a mixture of He (containing 2000 ppm DME) and H_2, where $H_2/He = 8$. The product stream was analyzed by GC at different times for a total of 10 h.

While not addressed in this paper, it is obvious that, with the formation of DME, water is also formed in equal molar amounts. At its low partial pressure relative to that of CO as extant in this study, it is doubtful that it had much of an effect on the Pd surface. However, it certainly could compete with MeOH and DME for sorption sites on the Al_2O_3. The SSITKA measurements allow us, thus, to determine the carbon adsorption/reaction trajectories in the presence of this by-product of DME synthesis.

Table 1 summarizes the results pertinent to this work from another study (25) of CO hydrogenation on the Pd/SiO_2 catalyst by itself at 220°C and 1.8 atm for different reactant flow rates after 10 h of reaction, corresponding to steady-state reaction conditions. The highest CO conversion under the conditions utilized here was less than 1%, allowing differential reaction conditions to be assumed. Based on the fact that 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) and the appropriateness of the apparent activation energy of MeOH (62 ± 4 kJ/mol), it can be concluded that MeOH synthesis was limited by reaction kinetics and not by thermodynamics or mass/heat transport. The selectivity for MeOH formation on Pd/SiO_2 was 98% for all the different flow rates used, and no DME formation was detected. The increase in rate with flow rate is due to the decrease in P_{MeOH}. The rate of MeOH synthesis is negative order (−0.15) in P_{MeOH} for the conditions used here (25).

SSITKA was used to determine the average surface residence times and concentrations of the active MeOH intermediates [see Ref. (19) for a review of the methodology]. Readsorption has been found to have a significant effect on the value of τ_{MeOH} obtained, as reported elsewhere (25–27). Its impact on N_{MeOH} is less important unless one tries to relate N_{MeOH} to the number of active sites. We have found (26) that, by extrapolating τ_{MeOH} to zero space time, a more accurate estimation of MeOH surface residence time for MeOH intermediates during synthesis (τ^0_{MeOH}) can be determined. This procedure acts to remove the effect of interparticle readsorption. However, τ^0_{MeOH} is still a slight overestimation of the value for τ_{MeOH} of surface reaction due to possible readsorption within the pores where primary reaction occurred. τ^0_{MeOH} was determined to be ca. 91 sec. The number of active intermediates was ca. 6.6 μmol/g of Pd/SiO_2. The number of Pd surface atoms, on the other hand, as determined by irreversible CO adsorption at room temperature, was 80 μmol/g. Thus, the surface coverage in very active reaction intermediates was ca. 0.08, assuming one MeOH intermediate per surface Pd atom. This degree of surface coverage is very typical for active intermediates during CO hydrogenation on Ru, Ni, and Co as determined by SSITKA.

TABLE 1

Reaction and SSITKA Results for MeOH Synthesis on $Pd + SiO_2$[a,b]

Catalyst configuration	Total reactant flow rate (cc/min)	% CO conversion	Total rate of CO conversion[c] (μmol/sec/g of Pd/SiO_2)	% CH_4 selectivity (carbon basis)	% MeOH selectivity (carbon basis)	P_{MeOH} in effluent (Pa)	τ_{MeOH}[d] (sec)	N_{MeOH} (μmol/g of Pd/SiO_2)
50 mg of Pd/SiO_2[a] (26)	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
Physical mixture of 50 mg of Pd/SiO_2 + 50 mg of SiO_2	18	0.26	0.071	2	98	52	164	11.4
	27	0.18	0.075	2	98	37	145	10.7
	36	0.15	0.079	2	98	29	131	10.1
	45	0.12	0.084	2	98	24	119	9.8

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

[b] % DME selectivity 0.

[c] Maximum error ±5%.

[d] Maximum error ±3 sec.

TABLE 2

Reaction and SSITKA Results for MeOH Synthesis on a Physical Mixture of $Pd/SiO_2 + Al_2O_3$[a]

No. of milligrams of Al_2O_3 in a physical mixture with 50 mg of Pd/SiO_2	Total flow rate (cc/min)	% CO conversion	Total rate of CO conversion[b] (μmol/sec/g of Pd/SiO_2)	% MeOH selectivity (carbon basis)	% DME selectivity (carbon basis)	P_{MeOH} in effluent (Pa)	P_{DME} in effluent (Pa)	τ_{MeOH}[c] (sec)	τ_{DME}[d] (sec)	τ_{Acid} (sec)	N_{MeOH} (μmol/g of Pd/SiO_2)	N_{Acid} (μmol/g of Al_2O_3)
50	18	0.25	0.067	80	18	41	5	154	173	19	10.1	0.1
	27	0.17	0.071	80	18	28	3	136	153	17	9.5	0.1
	36	0.13	0.073	79	19	21	3	125	141	16	8.9	0.1
	45	0.11	0.076	79	19	18	2	115	130	15	8.6	0.1
100	18	0.21	0.058	59	39	25	8	140	174	34	8.0	0.2
	27	0.15	0.062	60	38	18	6	124	154	30	7.5	0.2
	36	0.12	0.065	59	39	14	5	116	143	27	7.4	0.2
	45	0.10	0.069	61	37	12	4	109	133	24	7.4	0.2
50 followed by 50 mg of SiO_2 (dual bed)	18	0.24	0.065	80	19	39	5	161	181	20	10.4	0.1
	27	0.17	0.068	79	20	27	3	144	162	18	9.7	0.1
	36	0.13	0.071	79	20	21	3	130	157	17	9.1	0.1
	45	0.11	0.075	78	19	17	2	120	136	16	8.8	0.1

[a] For steady-state reaction (after 10 h) at 220°C, 1.8 atm, and $H_2/CO = 8$. CH_4 selectivity was equal to 2% for all conditions used.
[b] Maximum error ±5%.
[c] Maximum error ±3 sec.
[d] Maximum error ±3 sec.

Table 1 also contains the SSITKA results for MeOH synthesis over a composite catalyst mixture containing 50 mg Pd/SiO_2 and 50 mg SiO_2 at 220°C, 1.8 atm, and various reactant flow rates. Comparing the results in Table 1, it can be concluded that MeOH adsorbed at most slightly on SiO_2, as evidenced by the slight increase in τ_{MeOH} (considering the experimental error reported) for fixed reaction conditions, total reactant flow rate, and P_{MeOH}. The number of MeOH molecules adsorbing on SiO_2 appears to have been at most ca. 0.8 μmol/g of SiO_2, determined from the difference between N_{MeOH} for $Pd/SiO_2 + SiO_2$ and Pd/SiO_2 alone.

Table 2 contains the results of CO hydrogenation on the composite catalyst (a physical mixture of 50 mg of Pd/SiO_2 and 50 mg of Al_2O_3) for steady-state reaction at 220°C, 1.8 atm (1.6 atm H_2 and 0.2 atm CO), and different flow rates. For this composite catalyst, the carbon selectivity for oxygenate formation (both MeOH and DME) was constant (98%) for the various flow rates, while the carbon selectivity for DME was in the range of 18–19%.

Figure 1 shows a typical set of normalized isotopic transients for DME ($(^{12}CH_3)_2O$), MeOH ($^{12}CH_3OH$), and Ar obtained by switching between a stream containing ^{12}CO and Ar and another stream containing ^{13}CO under steady-state reaction (flow rate of 36 cc/min). Table 2 shows the results for both τ_{MeOH} and τ_{DME} at steady state for different reactant stream flow rates. As was the case for τ_{MeOH} on Pd/SiO_2, both τ_{MeOH} and τ_{DME} decreased with an increase in the flow rate due to a decrease in interparticle readsorption.

For the composite catalyst ($Pd/SiO_2 + Al_2O_3$) DME is produced in a secondary reaction of MeOH on acid sites on the γ-Al_2O_3. Because of this, in order to accurately determine the number of surface intermediates contributing to the formation of MeOH on the active surface of the Pd/SiO_2 catalyst, N_{MeOH} must be calculated by the multiplication of τ_{MeOH} by the rate of reaction of CO to form all the

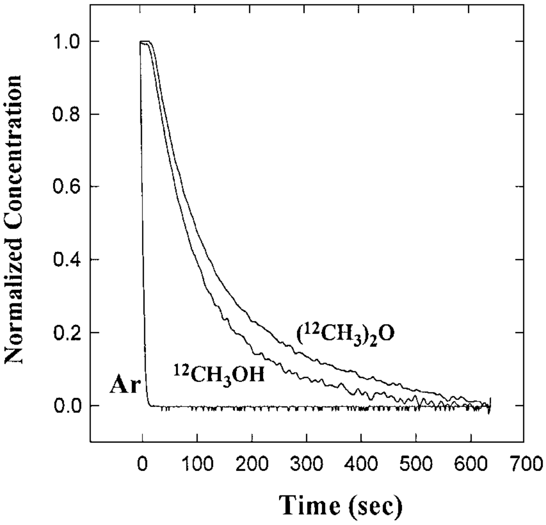

FIG. 1. Typical isotopic transients of $(^{12}CH_3)_2O$, $^{12}CH_3OH$, and Ar at steady-state during MeOH synthesis on a physical mixture of Pd/SiO_2 and Al_2O_3.

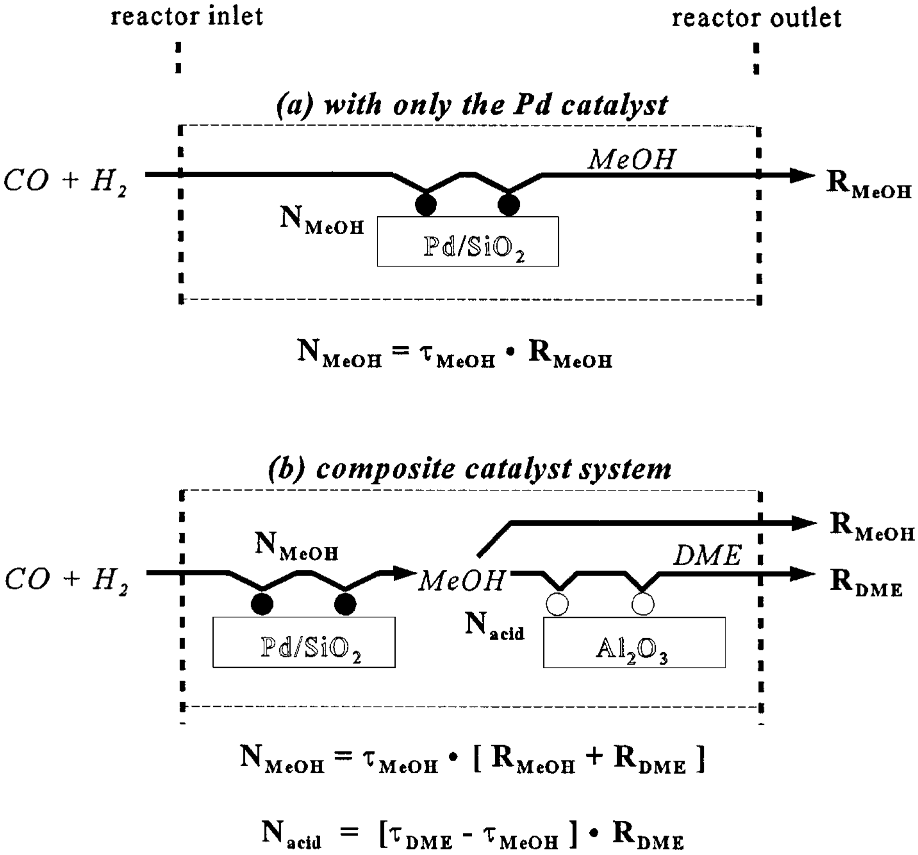

FIG. 2. A schematic showing the relationships between the surface parameters (τ_i and N_i) for MeOH and DME synthesis in single- and multifunctional catalyst systems.

oxygenates rather than by only the rate of MeOH eluting from the reactor. Figure 2 is a schematic representation of the relationship of N_{MeOH} to the rate of formation of MeOH and DME in the presence or absence of γ-Al_2O_3. Thus, N_{MeOH} for the composite catalyst system ($Pd/SiO_2 + Al_2O_3$) must be calculated according to the equation

$$N_{\mathrm{MeOH}} = [R_{\mathrm{MeOH}} + R_{\mathrm{DME}}] * \tau_{\mathrm{MeOH}} = R_{\mathrm{Oxygenates}} * \tau_{\mathrm{MeOH}},$$

where R_{MeOH} and R_{DME} represents the rates of conversion of CO to MeOH and to DME, respectively.

The value of N_{MeOH} determined (see Table 2) overestimates the number of primary reaction intermediates due to readsorption. This can be corrected somewhat by extrapolating N_{MeOH} to zero space time. Comparing the results in Tables 1 and 2 one can see that τ_{MeOH} was almost constant for either Pd/SiO_2 alone (Table 1) or mixed with Al_2O_3 (Table 2) for a given flow rate. This implies that τ_{MeOH} did not increase even though there were more sites available for MeOH adsorption, namely, the acid sites of Al_2O_3. This suggests that MeOH adsorbs almost irreversibly on Al_2O_3 and reacts to form DME. The slight decrease in τ_{MeOH} with the presence of Al_2O_3 is mainly due to experimental error or possibly due to the decrease in P_{MeOH} (due to reaction to DME) that might have decreased somewhat the average probability of readsorption of MeOH on Pd sites.

Because DME is produced by dehydration of MeOH on the acid sites (11, 12), it is more precise, in our opinion, to reflect the strength and the features of the active sites/intermediates for this reaction by identifying relevant SSITKA parameters as τ_{Acid} and N_{Acid}. CO and H_2 reacts on the active sites of Pd forming MeOH followed by its desorption and readsorption on acid sites where the formation of DME occurs. Hence, the average surface residence time of detected DME species (τ_{DME}) actually consists of the sum of two parameters: the average surface residence time of intermediates leading to MeOH on the active sites of Pd/SiO_2 (τ_{MeOH}) plus the average surface residence time of intermediates leading to DME on the acid sites of Al_2O_3 (τ_{Acid}). The average surface residence time of the species leading to DME on the acid sites (τ_{Acid}), thus, can be calculated using the equation

$$\tau_{\mathrm{Acid}} = \tau_{\mathrm{DME}} - \tau_{\mathrm{MeOH}}.$$

By multiplying τ_{Acid} by the rate of formation of DME, N_{Acid} can be calculated (taking into account that DME involves two carbons). Table 2 contains the calculated values of both τ_{Acid} and N_{Acid} for the composite catalyst ($Pd/SiO_2 + Al_2O_3$). These results seem to indicate (by varying the space time) that for low conversions of MeOH to DME, readsorption had at most only a small effect on the SSITKA parameters obtained for the acid sites. τ_{Acid} was significantly smaller than τ_{MeOH}. This indicates that the formation of DME from MeOH is much faster than MeOH synthesis.

The results of experiments to determine the reactivity of DME under these reaction conditions on acid and metal sites indicate that DME did not form detectable amounts of any product on Pd/SiO_2 in the presence of large amounts of H_2, such as exists during MeOH synthesis, even when CO was not present. Although DME can decompose to form MeOH on Al_2O_3 even in the presence of a large partial pressure of H_2, this reaction did not occur significantly on Al_2O_3 at 220°C and a P_{DME} similar to that present during MeOH synthesis. Only 3% of DME was able to react under conditions approximating those during synthesis. This indicates that, during MeOH synthesis on the composite catalyst ($Pd/SiO_2 + Al_2O_3$), the formation of DME as a secondary product can be considered essentially irreversible in the differential reactor used. Thus, τ_{MeOH} contains little dependence on DME surface residence times.

Although a comparison of the results of Tables 1 (Pd/SiO_2) and 2 ($Pd/SiO_2 + 50$ mg Al_2O_3) would suggest that the formation of DME did not affect the total rate of MeOH synthesis, doubling the amount of Al_2O_3 (see Table 2 for $Pd/SiO_2 + 100$ mg Al_2O_3) in the catalyst mixture resulted in a small decrease in the total rate of CO conversion. Thus, when DME is produced in large enough quantities, it would seem to compete somewhat for adsorption on the active sites of the Pd/SiO_2 catalyst. By comparing the results of Table 2 for 50 vs 100 mg of Al_2O_3, it can be suggested that DME readsorbs reversibly on the acid sites, as evidenced by the almost doubling of τ_{Acid} upon doubling the amount of Al_2O_3. The seeming invariance of N_{Acid} with flow rate in Table 2, on the other hand, was probably due to its low value and experimental error. The increase in the number of acid sites occupied by DME intermediates (per gram of Al_2O_3) upon increasing the amount of Al_2O_3 suggests that the acid sites were not totally saturated due to the low values of P_{DME} and P_{MeOH}.

Table 2 also contains the reaction and SSITKA results for MeOH synthesis over a dual bed consisting of a physical mixture of 50 mg of Pd/SiO_2 and 50 mg of Al_2O_3 followed by 50 mg of SiO_2. A comparison of all the results given in Table 2 indicates that DME does not adsorb significantly on SiO_2 as evidenced by the lack of any significant changes in the values of both τ_{Acid} and N_{Acid} in the presence of additional SiO_2 sites.

While TPD of DME or MeOH from Pd/SiO_2 and Al_2O_3 offer some possibilities for evaluating the adsorption strengths of these molecules on these catalysts, the results would not be directly extrapolatable to a multicomponent mixture under reaction conditions. Isotopic tracing allows an imperfect but better analysis for what is the case under steady-state reaction.

The analysis of sequential reactions in a multisite environment has been addressed using steady-state isotopic transient kinetic analysis. The system studied was methanol (MeOH) synthesis over monfunctional and bifunctional composite catalysts (Pd/SiO_2 and γ-Al_2O_3) at 220°C, 1.8 atm, and with $H_2/CO = 8$. MeOH synthesis took place, of course, only on active Pd sites. While MeOH is able to readsorb on Pd sites, it was found to adsorb at most only slightly on SiO_2 and almost irreversibly on Al_2O_3, forming dimethyl ether. Under the conditions utilized, DME was not very reactive on either the metal or the acid sites. In addition, DME was found to exhibit little adsorption on either Pd or SiO_2 sites. However, DME was found to readsorb reversibly on the acid sites of Al_2O_3. Accurate estimates were determined for the concentration of MeOH surface intermediates (on the Pd sites), N_{MeOH}, and that of DME intermediates (on the acid sites), N_{Acid}, as well as their respective surface residence times for reaction, τ_{MeOH} and τ_{Acid}, respectively. The surface coverage in very active MeOH intermediates on the Pd surface was ca. 0.08. The amount of active active sites on the Al_2O_3 being utilized at any time was ca. 0.1–0.2 μmol/g Al_2O_3. The formation of DME from MeOH was found to be a much faster reaction than the synthesis of MeOH, as evidenced by the fact that τ_{Acid} was much smaller than τ_{MeOH}. Due to the low P_{MeOH} resulting during differential reaction, the acid sites did not appear to be totally saturated.

This investigation resulted in the development of isotopic transient kinetic analysis for sequential reactions in a bifunctional catalyst system. The results show that, by using various catalyst configurations, determination of the surface reaction parameters for the different types of reactions and reaction sites can be made.

ACKNOWLEDGMENTS

Funding of this work was by the National Science Foundation (Grant No. CTS-9312519). S.H.A. gratefully acknowledges the support of the University of Kuwait.

REFERENCES

1. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52**, 157 (1978).
2. Driessen, J. M., Poels, E. K., Hindermann, J. P., and Ponec, V., *J. Catal.* **82**, 26 (1983).
3. Ichikawa, S., Poppa, H., and Boudart, M., *J. Catal.* **91**, 1 (1985).
4. Sudhakar, C., and Vannice, M. A., *J. Catal.* **95**, 227 (1985).
5. Kelly, K. P., Tatsumi, T., Uematsu, T., Driscoll, D. J., and Lunsford, J. H., *J. Catal.* **101**, 396 (1986).
6. Kikuzono, Y., Kagami, S., Naito, S., Onishi, T., and Tamaru, K., *Faraday Discuss Chem. Soc.* **72**, 135 (1982).

7. Hicks, R. F., and Bell, A. T., *J. Catal.* **90**, 205 (1984).
8. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73**, 237 (1982).
9. Cavalcanti, F. A. P., Stakheev, A. Yu., and Sachtler, W. M. H., *J. Catal.* **134**, 226 (1992).
10. Ryndin, Yu. A., Hicks, R. F., and Bell, A. T., *J. Catal.* **70**, 287 (1981).
11. Matsushima, T., and White, J. M., *J. Catal.* **44**, 183 (1976).
12. Derouane, E. G., Dejaifve, P., and Nagy, J. B., *J. Mol. Catal.* **3**, 453 (1977).
13. Biloen, P., *J. Mol. Catal.* **21**, 17 (1983).
14. Bennett, C. O., *in* "Catalysis Under Transient Conditions" (A. T. Bell and L. L. Hegedus, Eds.), ACS Symposium Series, Vol. 178, p. 1. Am. Chem. Soc., Washington, DC, 1982.
15. Happel, J., *Chem. Eng. Sci.* **33**, 1567 (1978).
16. Winslow, P., and Bell, A. T., *J. Catal.* **86**, 158 (1984).
17. Vada, S., Chen, B., and Goodwin, J. G., Jr., *J. Catal.* **153**, 224 (1995).
18. Hoost, T. E., and Goodwin, J. G., Jr., *J. Catal.* **137**, 22 (1992).
19. Shannon, S. L., and Goodwin, J. G., Jr., *Chem. Rev.* **95**, 667 (1995).
20. Yang, C. H., Soong, Y., and Biloen, P., *J. Catal.* **94**, 306 (1985).
21. Hoost, T. E., and Goodwin, J. G., Jr., *J. Catal.* **134**, 678 (1992).
22. de Pontes, M., Yokomizo, G. H., and Bell, A. T., *J. Catal.* **104**, 147 (1987).
23. Koranne, M. M., Goodwin, J. G., Jr., and Marcelin, G., *J. Catal.* **148**, 378 (1994).
24. Kazi, A. M., Chen, B., Goodwin, J. G., Jr., Marcelin, G., Rodrigez, N., and Baker, R. T. K., *J. Catal.* **157**, 1 (1995).
25. Ali, S. H., and Goodwin, J. G., Jr., *J. Catal.*, in press.
26. Ali, S. H., and Goodwin, J. G., Jr., *J. Catal.*, in press.
27. Vada, S., and Goodwin, J. G., Jr., *J. Phys. Chem.* **99**, 9479 (1995).

S. H. Ali
J. G. Goodwin, Jr.[1]

Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, Pennsylvania 15261

Received January 22, 1997; revised June 6, 1997; accepted June 18, 1997

---

[1] To whom correspondence should be addressed.