JOURNAL OF CATALYSIS **123,** 270–274 (1990)

NOTES

Nitroethane as a Probe Molecule for CO Hydrogenation over Ru/SiO$_2$

I. INTRODUCTION

Studies of $C_2H_5NO_2$ hydrogenation and addition to CO hydrogenation over a Ru/SiO$_2$ catalyst have been carried out as part of a current effort by our group to investigate the usefulness of nitroparaffins as probe molecules capable of generating C_yH_x groups and to better understand the role of the latter in hydrocarbon formation during CO hydrogenation (*1, 2*). Nitroparaffins are potentially interesting probe molecules because their C–N bond dissociation energy is in general quite weak, 57 ± 2 kcal/mole, as compared to the other bonds in these molecules. Also, the decomposition of the nitro group seems likely to lead to by-products that do not severely poison the catalyst activity as may occur with other functional groups such as those containing halogen (*3*) and sulfur (*4*) atoms.

The fate of CH_x groups generated by CH_3NO_2 addition to CO hydrogenation over Ru/SiO$_2$ was discussed elsewhere (*1*). Among other observations, it was noted that during CH_3NO_2 addition the weight percent of the C2 fraction remained almost constant while there were major changes in the weight percent of the C1 and C3 through C6 hydrocarbon fractions. The results of this study were viewed as an indication that C_2 surface species may play a special role in chain growth initiation during hydrocarbon formation on Ru catalysts. Such a view has also been advanced by other authors (*5–7*). It has also been well documented that one of the major effects on CO hydrogenation of additional C_2 groups generated by C_2H_5OH (*8, 9*) and C_2H_4 (*10–12*) addition is their participation in hydrocarbon formation through chain growth initiation.

II. EXPERIMENTAL

In an attempt to probe the possible role of C_2 groups in chain growth initiation 1.65 vol% $C_2H_5NO_2$ was added to He : CO : H$_2$ mixtures at two molar ratios (Conditions **A,** 1 : 2 : 2; **B,** 1 : 1 : 3) flowing at 3 liters/h over 0.25 g of Ru/SiO$_2$ at 533 K and 1 atm. $C_2H_5NO_2$ (1.7 vol%) hydrogenation in He : H$_2$ (1 : 4 molar ratio) was also studied under the same conditions. The Ru/SiO$_2$ catalyst used had a Ru loading of 1.8 wt% and a Ru dispersion and particle size of 53% and 16 Å, respectively. Details regarding the reaction system and procedures, catalyst preparation and characterization, and product analysis have been given elsewhere (*1*).

III. RESULTS

The rates of product formation and product distributions for CO hydrogenation in the absence and presence of $C_2H_5NO_2$ after 5 min reaction are given in Table 1. The values of the chain growth probabilities, α, and the olefin-to-paraffin molar ratios for the C2 and C3 fractions in the products are also listed. Table 1 also gives the rates of formation of CO$_2$ and of CH_3CN, the only nitrogen-containing hydrocarbon product detected.

Table 1 shows that both rate and selectivity of CH_4 formation were significantly reduced upon $C_2H_5NO_2$ addition. It can also be seen that, in general, both of these variables increased by at least 25% for the C3

0021-9517/90 $3.00

TABLE I

Activity and Selectivity of Ru/SiO_2 for CO Hydrogenation in the Absence and Presence of $C_2H_5NO_2$

Carbon fraction	Condition **A**				Condition **B**			
	Without $C_2H_5NO_2$		With $C_2H_5NO_2$		Without $C_2H_5NO_2$		With $C_2H_5NO_2$	
	μg/min	wt%	μg/min	wt%	μg/min	wt%	μg/min	wt%
C1	165.3	71.5	102.7	56.3	401.4	82.5	300.6	73.5
C2	27.7	12.0	26.3	14.4	45.1	9.3	51.5	12.6
C3	19.6	8.5	32.9	16.2	24.1	5.0	33.2	8.1
C4	11.2	4.9	14.3	7.8	10.3	2.1	15.4	3.8
C5	6.1	2.7	7.7	4.2	4.5	0.9	6.9	1.7
C6	1.4	0.6	1.8	1.0	1.1	0.2	1.3	0.3
Total	231.3		185.7		486.5		408.9	
CO_2[a]	11.9		164.5		10.5		105.6	
CH_3CN[a]	—		188.7		—		56.7	
Conversion[b]	1.8		—		7.5		—	
TOF[c]	10.7		—		22.3		—	
α	0.33		0.33		0.29		0.28	
C_2H_4/C_2H_6[d]	0.023		0.395		0.004		0.044	
C_3H_6/C_3H_8[d]	0.376		7.072		0.050		0.851	

Note. Reaction conditions: (**A**) He : CO : H_2 = 1 : 2 : 2; (**B**) He : CO : H_2 = 1 : 1 : 3; 1.2 vol% $C_2H_5NO_2$; 533 K; 101 kPa; GHSV = 3800 h^{-1}.

[a] μg/min.

[b] Conversion in (percent) based on hydrocarbon products formed.

[c] Turnover frequencies in ($s^{-1} \times 10^3$) based on volumetric hydrogen chemisorption.

[d] Molar ratio.

through C6 carbon fractions in the presence of $C_2H_5NO_2$. However, while the selectivity to C2 products increased by a similar amount, the rate of C2 product formation remained relatively unchanged. Furthermore, it can also be seen that there is a lack of significant change in the value of α upon $C_2H_5NO_2$ addition. Increases by at least one order-of-magnitude in the amount of CO_2 produced and in the olefin : paraffin molar ratios for the C2 and C3 carbon fractions were also observed. The total amounts of hydrocarbons produced decreased by about 20% when $C_2H_5NO_2$ was added, largely as the result of lower CH_4 production.

Another change that occurred upon $C_2H_5NO_2$ addition was the appearance of acetonitrile, CH_3CN, in the products. The amount of CH_3CN produced differed greatly for conditions **A** and **B**, corresponding to 24 and 7%, respectively, of the total number of moles of $C_2H_5NO_2$ added. The unreacted $C_2H_5NO_2$ found in the products did not exceed 7% of the $C_2H_5NO_2$ in the reactants for either condition **A** or **B**. The catalyst deactivated about 10% faster from 2 to 5 min when $C_2H_5NO_2$ was added to the reactants.

The hydrogenation of $C_2H_5NO_2$ in the absence of CO after 5 min on stream led to hydrocarbon products that consisted of 86.7 wt% CH_4, 13.3 wt% C_2H_6, and traces of C_3H_8 (<85 ppm vol). This corresponded to a conversion of 40% of the carbon originating from $C_2H_5NO_2$. No CO_2 or CH_3CN was detected in the products and only 3% of the original $C_2H_5NO_2$ appeared unreacted in the products. N_2 was the only compound detected in the products that contained nitrogen atoms. A carbon balance for $C_2H_5NO_2$ hydrogenation indicated that a large portion of its carbon did not appear as hydrocarbons or as unreacted $C_2H_5NO_2$ in the products, similar to the behavior observed for CH_3NO_2 addition (*1*).

IV. DISCUSSION

The observed increases in the absolute amount of higher hydrocarbons in the products when $C_2H_5NO_2$ was added can only be accounted for by increases in the rates of both chain initiation and chain growth. Furthermore, the fact that this occurred while there were no significant changes in the values of α also indicates that these two rates were increased by a similar amount. In the absence of CO, hydrogenation of $C_2H_5NO_2$ clearly indicates that a substantial portion of the C_2H_x fragments derived from the breaking of the C–N bond in $C_2H_5NO_2$ underwent hydrogenolysis to yield one-carbon CH_x units that ended up as CH_4, whereas the remaining two-carbon C_2H_x units were hydrogenated to form C_2H_6. It has been shown that incorporation of CH_x groups derived from CH_3NO_2 into the hydrocarbon formation pathway preferentially increased the rate of chain growth over the rate of chain initiation, even though both rates were observed to increase (*1*). The CH_x groups derived from the hydrogenolysis of C_2H_x groups generated by $C_2H_5NO_2$ addition to CO hydrogenation should behave similarly to those derived from CH_3NO_2, especially since CH_3NO_2 and $C_2H_5NO_2$ addition had similar effects on the hydrogenation ability of the catalyst as indicated by similar increases in the olefin-to-paraffin ratios. Therefore, the suggestion that rate of chain initiation is increased by as much as the rate of chain growth during $C_2H_5NO_2$ addition appears to be related to the fact that this probe molecule is also capable of generating additional two-carbon C_2H_x units. As previously mentioned, the formation of a C_2 surface intermediate has been proposed as being the rate-determining step in higher hydrocarbon formation over Ru catalysts (*5–7*).

It is interesting to compare the results presented here with those reported by Jordan and Bell (*10*) in an extensive study of the influence of added ethylene on the hydrogenation of CO over a Ru/SiO_2 catalyst. These authors reported that the addition of C_2H_4 resulted in a decrease in the rate of CH_4 formation while the rate of formation of C3+ hydrocarbons increased. For the addition of 5.4 vol% C_2H_4 to the reactants, their results also suggested that a significant fraction of the products incorporated single carbon units derived from C_2H_4 hydrogenolysis, as indicated by the methane produced, of which only 37% was derived from CO. The results presented here for the fate of CH_x and C_2H_x groups generated by $C_2H_5NO_2$ decomposition are consistent with their observations. Our previous results with the addition of ^{13}C-labeled CH_3NO_2 and the results reported by Jordan and Bell for C_2H_4 addition provide support for the suggestion that CH_x and C_2H_x groups derived from $C_2H_5NO_2$ were incorporated into growing hydrocarbon chains derived from CO hydrogenation.

The large increases observed in the olefin : paraffin ratios for the C2 and C3 carbon fractions seem to be the result of a lower hydrogenation ability of the catalyst as also indicated by the decrease in CH_4 production upon $C_2H_5NO_2$ addition. As mentioned before, a similar behavior was also observed with CH_3NO_2 addition (*1*). This lower hydrogenation ability of the Ru/SiO_2 catalyst is likely to be due to a lower surface coverage of hydrogen. This, in turn, could be the result of the additional competition of groups generated by $C_2H_5NO_2$ decomposition for sites normally occupied by hydrogen. Electronic effects caused by nitroparaffin addition to the surface of the catalyst have been considered (*1*) but seem unlikely, especially since the data show no evidence of groups such as $-NO_2$ on the surface. Therefore, it appears that the observed increases in the olefin : paraffin ratios reflect the displacement of hydrogen by additional carbon-containing groups generated by $C_2H_5NO_2$ decomposition.

The observed enhancement in CO_2 production upon $C_2H_5NO_2$ addition is similar to that observed for CH_3NO_2 addition and has been discussed in detail elsewhere (*1*). In that study, all of the carbon in the CO_2 originated from CO and not from the added probe molecule. This led to the suggestion that the additional CO_2 was formed by reactions of products from the decomposition of the NO_2 groups, namely H_2O and NO, with adsorbed CO molecules not directly involved in hydrocarbon formation which are thought to cover a large portion of the metal surface (*13, 14*). The main nitrogen-containing product from NO_2 decomposition was N_2 as indicated by the hydrogenation of $C_2H_5NO_2$.

Another feature of $C_2H_5NO_2$ addition to CO hydrogenation was the formation of significant amounts of CH_3CN. However, a comparison of the product distributions for conditions **A** and **B** in Table 1 shows that this product, whether present in small or significant amounts, did not influence the CO hydrogenation characteristics of the catalyst. It appears that CH_3CN formation occurs through the incomplete decomposition of the nitro group in $C_2H_5NO_2$. The fact that no CH_3CN was observed in the products during $C_2H_5NO_2$ hydrogenation may reflect a much higher surface coverage of hydrogen during this reaction compared to that during CO hydrogenation. An increase in the extent of C–N bond breaking in $C_2H_5NO_2$ with increasing hydrogen coverage would also explain the observation that a much smaller amount of CH_3CN was produced when the $CO : H_2$ was 1 : 3 compared to 1 : 1.

A significant amount of the carbon introduced as $C_2H_5NO_2$ did not appear as hydrocarbons or as unreacted $C_2H_5NO_2$. A large deposition of carbon on the Ru particles appears unlikely since the catalyst deactivated only slightly faster in its presence. The "missing" $C_2H_5NO_2$ is probably the result of interactions between this nitroparaffin and the SiO_2 support. Various degrees and types of interactions between CH_3NO_2 and SiO_2, Al_2P_3 and α-Mn_3O_4 have been shown to take place (*15*).

V. CONCLUSIONS

In situ addition of $C_2H_5NO_2$ to CO hydrogenation over Ru/SiO_2 resulted in the formation of both one- and two-carbon intermediates on the surface of the catalyst. The results presented here suggest that the C_2H_x groups derived from $C_2H_5NO_2$ played an important role in enhancing chain initiation for higher hydrocarbon formation. $C_2H_5NO_2$ also underwent hydrogenolysis of the C–C bond to generate CH_x groups that entered the hydrocarbon formation pathway in a manner similar to those derived from CH_3NO_2 as shown previously (*1*). The degree of scission of the C–N bond in $C_2H_5NO_2$ appeared to depend on the surface coverage of hydrogen. Use of $C_2H_5NO_2$ as a probe molecule without significant perturbation of the CO hydrogenation reaction again demonstrated the utility of nitroparaffins as a potential source of C_yH_x groups for mechanistic studies of CO hydrogenation.

ACKNOWLEDGMENT

Funding from the National Science Foundation under the Presidential Young Investigator Program (CBT-8552656) is gratefully acknowledged.

REFERENCES

1. Cavalcanti, F. A. P., Oukaci, R., Wender, I., and Blackmond, D., *J. Catal.* **123,** 260 (1990).

2. Cavalcanti, F. A. P., Ph.D. dissertation, University of Pittsburgh, 1989.

3. Cavalcanti, F. A. P., Blackmond, D. G., Oukaci, R., Sayari, A., Erdem-Senatalar, A., and Wender, I., *J. Catal.* **113,** 1 (1988).

4. Chuang, S. S. C., and Pien, S. I., *Catal. Lett.*, in press.

5. Mims, C. A., McCandlish, L. E., and Melchior, M. T., *Catal. Lett.* **1,** 121 (1988).

6. McCandlish, L. E., *J. Catal.* **83,** 362 (1983).

7. Joyner, R. W., *Catal. Lett.* **1,** 307 (1988).

8. Kummer, J. T., Podgurski, H. H., Spencer, W. B., and Emmett, P. H., *J. Amer. Chem. Soc.* **73,** 564 (1951).

9. Tau, L-M., Dabbagh, H., Bao, S., Chawla, B.,

Halasz, J., and Davis, B. H., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips, and M. Ternan, Eds.), Vol. 2, p. 861. Chem. Institute of Canada, Ottawa, 1988.
10. Jordan, D. S., and Bell, A. T., *J. Phys. Chem.* **90,** 4797 (1986).
11. Pichler, H., and Schultz, H., *Chem. Ing. Tech.* **42,** 1162 (1970).
12. Gibson, E. J., and Clarke, R. W., *J. Appl. Chem.* **11,** 293 (1961).
13. Winslow, P., and Bell, A. T., *J. Catal.* **86,** 158 (1984).
14. Dalmon, J. A., and Martin, G. A., *J. Catal.* **84,** 45 (1983).
15. Ponec, V., personal communication, 1989.

F. A. P. CAVALCANTI
R. OUKACI
I. WENDER
D. G. BLACKMOND[1]

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

Received October 18, 1989; revised December 20, 1989

---

[1] To whom correspondence should be addressed.