JOURNAL OF CATALYSIS **76**, 238–239 (1982)

Kinetic Isotope Effect in the Selective Oxidation of Methanol to Formaldehyde over Some Molybdate Catalysts

Over the years, several different rate-determining steps have been proposed by various researchers for the oxidation of methanol to formaldehyde over ferric molybdate/molybdenum trioxide catalysts. Desorption of the products (*1*), reoxidation of the catalyst surface (*2*), and reaction of methanol with surface oxygen (*3*) have been mentioned. Experimental techniques and conditions varied, and it was suggested (*1*) that especially the temperature could be an important factor causing the discrepancies.

In order to clarify this issue, we have investigated kinetic isotope effects using partially and fully deuterated methanol, CH_3OD, and CD_3OD. Four catalysts were tested: a commercial Harshaw preparation containing a 3:1 molar ratio of MoO_3 and $Fe_2(MoO_4)_3$, pure MoO_3, pure $Fe_2(MoO_4)_3$, and $FeMoO_4$. Surface areas varied from 2.3 m^2/g for MoO_3 to 6.1 m^2/g for $Fe_2(MoO_4)_3$. Reactants were CH_3OH (>99.5%, UltraR, Hopkins & Williams), CH_3OD (99% D, Stohler Isotope Chemicals), and CD_3OD (99% D, Merck Sharpe & Dohme Canada Limited). Typically 3 g of catalyst was used in a differential reactor with external recycle. Mass and heat transfer were rapid compared to the rate of reaction. The feed gas contained 2–20% methanol, 5–40% oxygen, and the balance nitrogen. Differential rates and selectivities were obtained under steady-state conditions over a wide range of conversions.

It is assumed (*4*) that the initial step in the reaction sequence is the dissociative adsorption of methanol to form a surface methoxy. This is in agreement with our product distributions which show dimethyl ether, methyl formate, and dimethoxymethane in addition to formaldehyde, carbon monoxide, and water, especially at low temperatures and low conversions. If the rate-limiting step is this dissociative adsorption of methanol, a kinetic isotope effect will be observed using either CH_3OD or CD_3OD. If the limiting step is the abstraction of a second hydrogen to form an adsorbed formaldehyde, there will be only an isotope effect in the case of CD_3OD. The ratios of the rate constants with the different methanol feeds were calculated (Table 1). The rate constants were obtained by fitting the data to a rate equation of the power law type.

The results clearly show that the rate-limiting step on all four catalysts is the abstraction of a hydrogen from the methyl group. This is also confirmed by changes in product distribution. CH_3OH and CH_3OD yield identical product distributions, but in the case of CD_3OD the selectivity to dimethyl ether increases by a factor of 4–6, and the selectivity to formaldehyde decreases. Selectivities to the other products are not very different and the slight changes can be explained by differences in methanol conversion. In order to make the ether, no carbon–hydrogen bonds need to be broken. The reason that the rate constants for CH_3OD are somewhat lower than those for CH_3OH is probably the fact that some of the surface hydroxyl groups now contain deuterium. The dehydroxylation of the surface, a process that creates the adsorption sites for methanol, apparently is more difficult when –OD as well as –OH groups are involved. Addition of water to the feed shows that water has an inhibiting effect on

0021-9517/82/070238-02$02.00/0

TABLE 1

Ratios of Rate Constants Using the Different Methanol Feeds

T (°C)	k_{CH_3OD}/k_{CH_3OH}	k_{CD_3OD}/k_{CH_3OH}	T (°C)	k_{CH_3OD}/k_{CH_3OH}	k_{CD_3OD}/k_{CH_3OH}
	Harshaw			$Fe_2(MoO_4)_3$	
220	0.93	—	200	0.90	0.30
230	0.92	0.26	229	0.85	0.25
260	0.94	0.37	250	0.83	0.28
			259	0.83	0.27
	MoO_3			$FeMoO_4$	
265	0.87	0.15	270	0.93	0.37
300	0.96	0.31			
335	0.93	0.37			

the reaction rate, presumably due to competitive adsorption.

In a related study (5) using a pulse reactor, it was shown that the rate-limiting step is the breaking of a carbon–hydrogen bond over a wide range of temperatures (200–400°C).

ACKNOWLEDGMENT

The authors wish to thank U. Chowdhry who prepared the pure phases of ferric and ferrous molybdate.

REFERENCES

1. Pernicone, N., Lazzerin, F., Liberty, G., and Lanzavecchia, G., *J. Catal.* **14,** 293 (1969).
2. Jiru, P., Wichterlova, B., and Tichy, J., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 199. Wiley, New York, 1965.
3. Popov, B., Osipova, K., Malakhov, V., and Kolchin, A., *Kinet. Katal.* **12**(6), 1464 (1971).
4. Edwards, J., Nicolaidis, J., Cutlip, M., and Bennett, C., *J. Catal.* **50,** 24 (1977).
5. Machiels, C. J., *in* "Catalysis under Transient Conditions" (A. Bell and L. Hegedus, Eds.), ACS Symposium Series, No. 178, p. 239. Amer. Chem. Soc., Washington, D.C., 1982.

C. J. Machiels
A. W. Sleight

Central Research and Development Department
E.I. du Pont de Nemours & Company
Experimental Station
Wilmington, Delaware 19898

Received October 19, 1981; revised March 1, 1982