

AMMOXIDATION OF ETHANE ON OXIDE CATALYSTS

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Received August 16, 1977

Accepted January 10, 1978

Ammonoxidation of ethane on chromium- and scandium-molybdenum oxide catalysts has been studied. The rate-determining step of acetonitrile formation is shown to be C-H bond breaking in n-paraffins.

Изучен окислительный аммонолиз этана на хроммолибденовом и скандий-молибденовом окисных катализаторах. Показано, что лимитирующей стадией реакции образования ацетонитрила является разрыв C-H связи в n-парафинах.

Little is known about the ammonoxidation of low molecular weight paraffins. Previous studies in this field were restricted to the ammonoxidation of propane to acrylonitrile /1, 2/.

The present paper reports on the ammonoxidation of ethane as well as some other low molecular weight paraffins on chromium- and scandium-molybdenum oxide catalysts.

EXPERIMENTAL

Cr-Mo-O and Sc-Mo-O (Cr/Mo = 1/1.5, Sc/Mo = 1/1.5) catalysts were coprecipitated from a mixture of ammonium paramolybdate and chromic nitrate or scandium nitrate, respectively, with a 10% ammonia solution by the technique described in Ref. /3/.

The specific surface area of the samples determined chromatographically from the thermodesorption of nitrogen is 20.3 and 8.4 m²/g for Cr-Mo-O and Sc-Mo-O, respectively.

Table 1
Ammonoxidation of ethane

Catalyst	Temperature of reactor	Time of contact (sec)	Con- version	Selectivity (%)				
				CO ₂	CO	HCN	C ₂ H ₃ N	
Cr-Mo-O	400	5.8	10.6	40.1	3.0	34.5	22.4	
		14.3	21.0	48.6	7.8	26.6	17.0	
		21.2	26.5	51.5	12.2	21.6	14.7	
		29.2	30.5	54.4	16.8	16.3	12.5	
	450	8.0	7.7	60.5	0.2	7.1	32.2	
		18.0	12.1	69.1	4.3	2.9	23.7	
21.9		13.4	68.1	7.0	1.9	23.0		
Sc-Mo-O	400	33.2	14.8	67.4	10.7	2.6	19.3	
		500	4.4	12.8	62.3	4.3	6.5	26.7
			11.0	17.3	71.1	9.2	3.4	16.3
	500	24.2	28.7	77.1	15.2	1.3	6.4	

A gradientless flow reactor with a vibro-fluidized catalyst bed was employed in the study. The chromatographic analysis of reactants and initial products was carried out on columns with NaX molecular sieves at room temperature, and Porapak-T with programmed heating of the column from 40 to 180 °C.

The initial mixture contains 5% R (R = CH₄, C₂H₆, C₂D₆, C₃H₈, n-C₄H₁₀ and iso-C₄H₁₀), 5% NH₃, 18% O₂, the rest being helium (vol. %). The tests were carried out at 400-500 °C

RESULTS AND DISCUSSION

Table 1 lists the results of catalyst tests. As seen from Table 1, the reaction yields acetonitrile, hydrocyanic acid, carbon monoxide and dioxide. The depen-

(5% C₂H₆, 5% NH₃, 18% O₂, 72% He)

W _{tot} × 10 ⁻¹⁰ (molec. C ₂ H ₆ /cm ² sec)	Rate × 10 ⁻¹⁰ (molec. C ₂ H ₆ /cm ² sec)			
	CO ₂	CO	HCN	C ₂ H ₃ N
16.1	6.5	0.50	5.60	3.5
13.0	6.3	1.00	3.50	2.2
11.0	5.7	1.30	2.40	1.6
9.3	5.1	1.60	1.50	1.1
19.9	12.1	0.04	1.40	6.36
13.9	9.6	0.60	0.40	3.30
12.7	8.6	0.90	0.24	2.96
9.3	6.3	1.00	0.20	1.80
59.8	37.3	2.58	3.90	16.02
32.6	23.1	3.00	1.11	5.39
24.6	19.0	3.74	0.32	1.54

dence of the selectivity on the conversion degree (Fig. 1) shows that the products of complete oxidation are formed sequentially as the result of consecutive oxidation of nitriles. The initial selectivity to nitriles reaches 75%.

During the formation of the products of complete oxidation of saturated hydrocarbons, C-H bonds are known to break in the rate-determining step. This leads to a significant kinetic isotope effect when substituting deuterium for protium /4/. The rates of ammoxidation of C₂H₆ and C₂D₆ have been compared on both catalysts to elucidate the character of the rate-determining step in the course of acetonitrile formation. Experimental results are given in Table 2. As is seen from the Table,

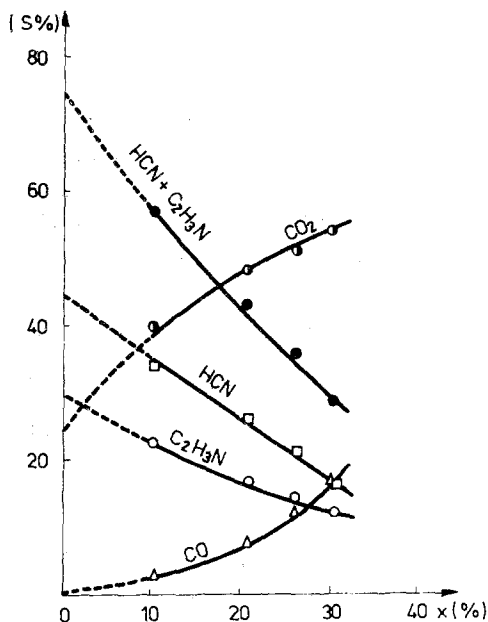


Fig. 1. Selectivity as a function of the conversion degree for ethane ammoxidation on a Cr-Mo-O catalyst ($T = 400^{\circ}\text{C}$)

a significant kinetic isotope effect is observed in the course of acetonitrile formation. Hence, C-H bonds break in the rate-determining step of this reaction.

C-H bond cleavage in ethane during acetonitrile formation may proceed either homolytically or heterolytically and is accompanied by the formation of carbanions or carbocations. As found by Burwell et al. /5/ for the rate of H-D exchange in low molecular weight paraffins, methane exchanges more rapidly than ethane, and the primary hydrogen atoms react faster than the secondary ones. On this basis the authors have concluded on the carbanion character of the alkyl intermediate.

We have measured and compared the rates of ammoxidation of a series of low molecular weight paraffins, including methane and compounds with primary, secondary and tertiary hydrogen atoms on a chromium-molybdenum catalyst. The results are listed in Table 3.

Table 2
Kinetic isotope effect in the ammoxidation of ethane (5% R, 5% NH₃, 18% O₂, 72% He)

Catalyst	Hydrocarbon	Temperature of reactor (°C)	Time of contact (sec)	Conversion, (%)	W _{tot} × 10 ⁻¹⁰ (molec. R/cm ² sec)	W _{tot} C ₂ D ₂ / W _{tot} C ₂ H ₆	W _{acetonitrile} × 10 ⁻¹⁰ (molec. R/cm ² sec)	$\frac{W_{C_2D_3N}}{W_{C_2H_3N}}$
Cr-Mo-O	C ₂ H ₆	400	10.7	18.3	16.3	0.724	2.77	0.408
	C ₂ D ₆				11.8		1.13	
Sc-Mo-O	C ₂ H ₆	450	10.7	6.3	13.0	0.620	3.90	0.462
	C ₂ D ₆				8.05		1.80	

Table 3
 Ammoxidation of low molecular weight alkanes (5% R, 5% NH₃, 18% O₂, 72% He)

Hydrocarbon	Time of contact (sec)	Con- version (%)	W tot. × 10 ⁻¹⁰ (molec. R/cm ² sec)	Rate × 10 ⁻¹⁰ (molec/cm ² sec)							
				CO ₂	CO	C ₃ H ₆ C ₃ H ₈	HCN	C ₂ H ₃ N	C ₃ H ₃ N	CH ₃ C ₃ H ₂ N	
CH ₄	11.1	1.82	1.34	1.34	-	-	-	-	-	-	-
C ₂ H ₆	14.3	21.0	13.0	12.6	2.0	-	7.0	2.2	-	-	-
C ₃ H ₈	12.0	19.4	14.6	19.5	6.0	-	6.6	3.75	1.4	-	-
H-C ₄ H ₁₀	11.8	21.2	15.1	19.2	9.6	0.8	10.4	3.6	0.5	-	-
iso-C ₄ H ₁₀	11.7	29.2	22.8	38.1	4.3	2.2	16.8	5.0	1.9	-	2.5

As is seen from Table 3, methane is oxidized much more slowly than ethane (in contrast to the results obtained for isotope exchange /5/). The overall transformation rates of compounds with primary and secondary hydrogen atoms are similar, while the rates of acetonitrile formation in compounds with secondary atoms are higher. Upon going to paraffins with a tertiary C-H bond, the rates of the overall reaction and acetonitrile formation increase significantly. The dependence observed is in contrast to that expected for the corresponding carbanions. Such a dependence may be observed either for homolytic C-H bond cleavage or for heterolytic dissociation resulting in the formation of carbocations.

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Acknowledgement. The authors thank T. M. Trubanova and M. M. Andrushkevich for the preparation of scandium molybdate samples.

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