REACTION KINETICS AND CATALYSIS LETTERS, Vol. 2, No. 3, 305–312 (1975)

CATALYTIC REACTIONS OF ACETONE ON $MoO_3 . Al_2O_3$

N. Giordano,* J. C. J. Bart, A. Vaghi

Montedison Research Laboratories, 20021 Bollater, Milano, and

V. Ragaini

Institute of Physical Chemistry, University of Milano, Italy

Received November 12, 1974

The interaction of acetone with $MoO_3 . Al_2O_3$ catalysts of low MoO_3 content (< 10 w/w %) yields mainly tri- and tetramethylbenezenes, as opposed to isobutane and CO or CO_2 in MoO_3-richer systems. The variations in product distribution with composition appear to be interpretable on the basis of the gradually changing surface acidity of the catalytic system; there is no need to assume differences in molybdenum coordination for explaining the results.

Взаимодействие ацетона с катализаторами $MoO_3 \cdot Al_2O_3$ с низким содержанием MoO_3 (<10 вес.%) приводит, в основном, к образованию три- и тетраметилбензолов, в противоположность системам с большим содержанием MoO_3, приводящим к образованию изобутена, CO и CO_2. Изменения в распределении продукта с составом можно обьяснить на основе постепенного изменения кислотности поверхности каталитической системы. Для обьяснения результатов, т.о., отпадает необходимость в предположении различия в координации молибдена.

---

* Present address: Montedison Research Laboratories, Priolo, Sicily,

INTRODUCTION

Previous reports from this Laboratory /1–6/ on the solid state properties of a series of $MoO_3 \cdot Al_2O_3$ catalysts (containing up to 30 w/w % MoO_3) have indicated the existence of two structurally distinct regions of composition characterized by tetrahedral (up to 10% MoO_3) and octahedral (at higher contents) oxomolybdenum configurations. It has turned out to be possible to establish a specific correlation with catalytic activity in the case of the reaction with propylene as, in fact, disproportionation occurs in the tetrahedral region and oxyhydration to acetone at higher MoO_3 compositions. The active sites were indicated to be Mo(V) pairs of the bis-molybdenyl type in the case of disproportionation and a combination of Mo(V)–Mo(VI) in octahedral coordination in the case of oxyhydration to acetone.

In this paper we wish to supplement our catalytic data by a further example of specificity in the class of $MoO_3 \cdot Al_2O_3$ systems, using acetone as a model reactant. In doing so, we aimed at studying whether the described differences in molybdenum coordination would affect the product distribution also in this case. Acetone was chosen as a reactant since it is known to form a great variety of products depending upon the nature of the catalyst /7/.

EXPERIMENTAL

Catalyst preparation and catalytic activity experiments were performed using the procedures and apparatus described elsewhere /1–6/. Before use the catalyst samples (0.25 g) were activated "in situ" in a flow of helium (40 cm^3/min) for 2 hrs at 500 °C. Interaction with 2 μl pulses of acetone was studied at 300 °C with or without the simultaneous injection of water. To allow for identification of all possible products, a preliminary set of experiments was performed by linking the gas-chromatographic unit (Fractovap Mod. C) to a mass spectrometer (Hitachi Perkin-Elmer RMU-6E). Quantitative results were collected from chromatographic records using a Poropak T/FFAP 5% column operated at 170 °C.

RESULTS

The mass-spectrometric analysis of the effluents is given in Table 1 and illustrates the product formation. The results indicate the existence of two distinct regions, the first of which is characterized by the presence of tri- and tetramethylbenzenes, further indicated as polymethylbenzene (PMB); at compositions higher than 10 w/w % MoO_3, isobutene prevails together with $CO_{\underline{x}}$. Besides these main components, there are minor amounts of methane, propylene, benzene, toluene and xylene.

Attempts to establish a more quantitative estimate of the various products were hampered by a large fraction of acetone being chemisorbed on the catalyst, however, an assessment of catalytic activity is still possible using values of conversion to observed products. Typical catalytic patterns are of the type illustrated in Fig. 1 for the conversions and Fig. 2 for the selectivities. As no great difference was observed as a function of the progressive number of slugs, the degree of reduction appeared to be irrelevant. Closer appraisal of the results collected in Figs. 1 and 2 shows: a) a low MoO_3 region (up to 8–10 w/w % MoO_3) characterized by a low overall activity and selectivities varying in the order: PMB > acetic acid > isobutene > $CO_{\underline{x}}$; b) a MoO_3 -rich region (from 10 w/w % MoO_3 onwards) characterized by a sharp increase of activity as a function of the composition and selectivities changing in the order: isobutene > $CO_{\underline{x}}$ > acetic acid, with PMB being almost absent.

Table 1

Mass-spectrometric analysis of the interaction of acetone with $MoO_3 \cdot Al_2O_3$

Samples

Sample (°)	Outgassing in He at 500 °C for 2 hrs	T_{exp} (°C)	No. of slug	Volume of slug (μl)		Products ($\underline{XX}$ = Main Products)
				Acetone	Water	
MoO_3-6-500	no	300	1	2	-	CH_4; C_3^-; iso C_4^-; xylenes; $\underline{PMB}$
			2	2	3	iso C_4^-; xylenes; $\underline{PMB}$
			3	2	5	Same
	yes	300	1	2	-	C_3^-; iso C_4^-; $\underline{PMB}$
	yes	300	1	2	1	C_3^-; iso C_4^-; xylenes; $\underline{PMB}$
			2	2	2	Same
MoO_3-20-500	no	300	1	2	-	$\underline{\text{iso } C_4^-}$; CO_x; C_3^-; toluene; xylenes
			2	2	3	Same
	no	400	3	2	-	$\underline{\text{iso } C_4^-}$; CO_x; C_3^-; benzene; toluene, xylenes; CH_4; C_2^+; C_2^-
MoO_3-30-500	yes	300	1	2	-	$\underline{\text{iso } C_4^-}$; $\underline{CO_x}$; C_3^-
	yes	300	1	2	1	$\underline{\text{iso } C_4^-}$; $\underline{CO_x}$; C_3^-; xylenes
			2	2	2	$\underline{\text{iso } C_4^-}$; $\underline{CO_x}$; xylenes

(°) Reference to the sample is made by MoO_3-W-T, where W indicates w/w % of MoO_3 and T the activation temperature (°C)

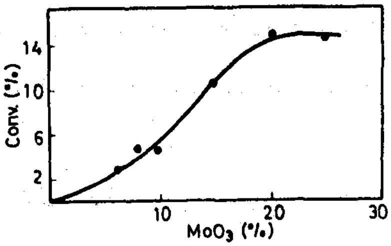


Fig. 1. Molar conversion vs. composition (w/w % MoO_3) for the first slug (for experimental conditions, see text)

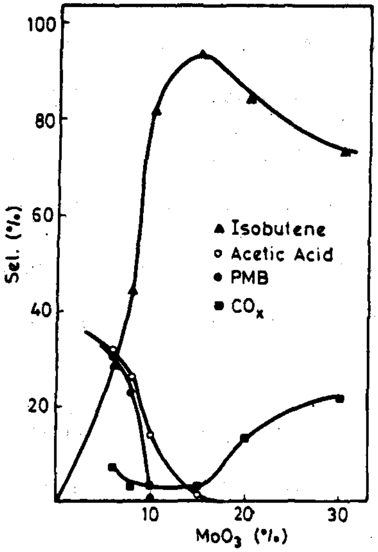


Fig. 2. Molar selectivities vs. composition (w/w % MoO_3) for the first slug (for experimental conditions, see text)

DISCUSSION

The following results are relevant to establishing a correlation between catalytic activity and solid state properties:

(i) PMB is formed from acetone under the influence of strong acidic media, such as concentrated H_2SO_4 /7/;

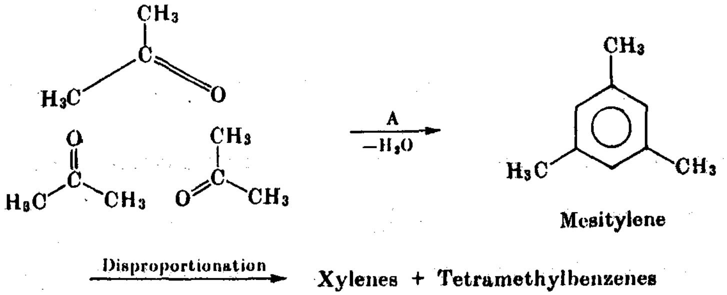
(ii) Diacetone alcohol is obtained via condensation of acetone in the presence of a base, while mesityl oxide is formed from the former product over bifunctional catalysts /8/;

(iii) Acetic acid may derive from water and ketene /9, 10/, the latter being obtained from mesityl oxide together with isobutene and from the reverse of the ketonization of acetic acid /11–13/;

(iv) As will be shown later /14/, the heat of immersion of $MoO_3 \cdot Al_2O_3$ catalysts in pyridine, hence the total acidity /15/, shows a fluctuating behaviour, with maxima (Max) an Minima (Min) as follows (the first figure is w/w % MoO_3, the second the heat of immerson in J/mg catalyst): 0, 3.1 (Max); 4, 0.6 (Min); 8, 5.0 (Max); 15, 0.7 (Min); 25, 2.8 (Max); 30, 1.6 (Min).

(v) As suggested elsewhere /1–6/, variations in molybdenum coordination with concentration must also play a role in the explanation of the behaviour of the MoO_3–Al_2O_3 system (Fig. 1).

We therefore derive the following picture. In the low MoO_3 region (<8–10 w/w % MoO_3), Fig. 2, isobutene, acetic acid, PMB and CO_x are present as significant products. Formation of PMB may occur on strongly acidic centers (A) present at low MoO_3 contents /14/

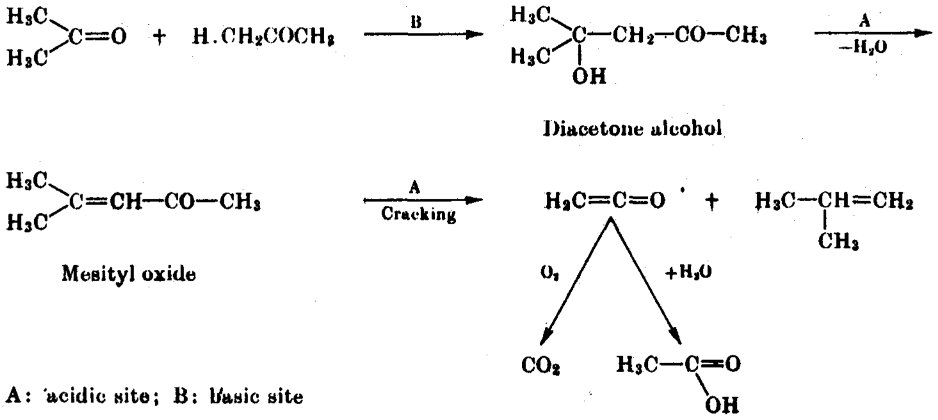


A: acidic site

The presence of the other products suggests that $MoO_3.Al_2O_3$ should accomodate both basic (B) and acidic centers (A), with a base B removing H^+ according to the equation

$$CH_3COCH_3 + B \longrightarrow {}^{-}CH_2COCH_3 + BH^+$$

resulting in the formation of a stabilized carbanion, which yields diacetone alcohol via attack of the carbonyl group of a second molecule of acetone. Further dehydration leads to mesityl oxide and isobutene, acetic acid and CO_2; the formation of acetic acid together with isobutene rules out the ketonization process as, in this event, only acetic acid is formed. The following scheme summarizes the above findings.



As mentioned above (point iv), in the MoO_3-rich region ($\geqslant 15$ w/w % MoO_3) acidic sites show a lower average strength than in the low MoO_3 region. Isobutene is the main reaction product without acetic acid and PMB. The larger fraction of CO_2 is probably indicative of some consecutive reaction involving ketene. In fact, apart from a reaction with water to give acetic acid, ketene may be oxidized to CO_2; the ratio of the two products may be related to the state of hydration of the surface.

REFERENCES

1. N. Giordano, A. Vaghi, J. C. J. Bart, A. Castellan: Proceedings of the Symposium on the Mechanism of Hydrocarbon Reactions. Siófok, June 5–7, 1973. Hungarian Academy of Sciences (in press)
2. N. Giordano, J. C. J. Bart, A. Castellan, A. Vaghi: J. Less Common Met., <u>36,</u> 367 (1974)
3. N. Giordano, J. C. J. Bart, A. Castellan, A. Vaghi, G. Martinotti: J. Catal. (in press)
4. N. Giordano, A. Castellan, J. C. J. Bart, A. Vaghi, F. Campadelli: J. Catal. (in press)
5. N. Giordano, M. Padovan, A. Vaghi, J. C. J. Bart, A. Castellan: J. Catal. (in press)
6. N. Giordano, A. Vaghi, J. C. J. Bart, A. Castellan: J. Catal. (in press)
7. L. F. Fieser, M. Fieser: Advanced Organic Chemistry, Reinhold Publishing Co., New York 1962
8. Z. N. Verkhovskaya, N. A. Klimenko, E. M. Zalesskaya, I. N. Bychkova: Khim. Prom. (Moscow) <u>43,</u> 500 (1967)
9. M. Ya. Kagan, V. B. Falkovsky: Dokl. AN SSSR, <u>2,</u> 131 (1947)
10. S. H. McAllister, Wm. A. Bailey, C. M. Bouton: J. Amer. Chem. Soc. <u>62,</u> 3210 (1940)
11. J. C. Kuriacose, R. Swaminathan: J. Catal., <u>14,</u> 348 (1969)
12. R. Swaminathan, J. C. Kuriacose: J. Catal., <u>16,</u> 357 (1970)
13. J. M. J. Wetzels: Int. Rep. Techn. Univ. Eindhoven, March 5, 1969
14. V. Ragaini, G. Materrese, N. Giordano, J. C. J. Bart: to be published.
15. R. L. Stone, H. F. Rase: Anal. Chem., <u>29,</u> 1273 (1957)