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Catalytic Oxidation of Olefins over Oxide Catalysts Containing Molybdenum

IV. Catalysts for the Oxidation of Propylene to Acetone

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Various metal oxides combined with molybdenum trioxide have been examined for their catalytic activities in the oxidation of propylene to acetone. In the molybdenum-poor series (10 at. % molybdenum), TiO_2–, Fe_2O_3–, and Cr_2O_3–MoO_3 as well as Co_3O_4–MoO_3 and SnO_2–MoO_3 reported previously, are active for the selective formation of acetone. V_2O_5–, NiO–, CuO–, and ZnO–MoO_3 are able to form acetone but with poorer selectivity. SnO_2–MoO_3 shows the highest activity among the effective catalysts.

An increase in molybdenum concentration decreases the catalytic activity for acetone formation in several of the binary systems. However, molybdenum-rich SnO_2–MoO_3 and TiO_2–MoO_3 catalysts (70 at. % molybdenum) show high activity and selectivity for acetone formation in common with the corresponding poor catalysts.

Tungsten trioxide or triuranium octoxide fails to be an effective component instead of molybdenum trioxide. Molybdenum trioxide seems to be an essential component for an active catalyst. Over any effective catalyst the reaction temperature to form acetone is far lower than that of the allylic oxidiation. No allylic oxidation product is formed under the reaction conditions at which acetone is mainly produced.

INTRODUCTION

The catalytic oxidation of olefins to produce ketones was first found by Smidt *et al.* using $PdCl_2$–$CuCl_2$ catalyst in aqueous solution (*1*) and has been developed in the Wacker process. However, in the heterogeneous oxidation of olefins over transition metal oxides, no catalyst effective in forming ketone was known prior to 1967 (*2–4*). Recently, Buiten has reported that acetone is one of the main products as well as acetic acid and acrolein in the oxidation of propylene over SnO_2–MoO_3 catalyst (*5*), and the present authors also have found that propylene is oxidized to acetone selectively over Co_3O_4–MoO_3 (*6*) and SnO_2–MoO_3 (*7*). In a further investigation, oxidations of various olefins over Co_3O_4–MoO_3 and SnO_2–MoO_3 were examined, and it was found that these two catalysts are also effective for the oxidations of normal butenes and 1-pentene to methyl ethyl ketone and methyl propyl ketone, respectively (*8*). A reaction mechanism which demonstrates that ketone is formed via hydration of olefin to form alcoholic intermediate followed by oxydehydrogenation was proposed for this oxidation (*8*).

In the present work, we examine the catalytic activities of some other binary oxides for the oxidation of propylene to acetone, since this reaction is the most typical of this type of oxidation.

EXPERIMENTAL

All runs were carried out using a conventional flow system at 1 atm of pressure. The apparatus and analytical method for reactants and products were the same as described previously (*6*).

Catalysts

The following salts were used as starting materials for the preparation of the oxide catalysts. Nitrates were used for iron, nickel, chromium, cobalt, zinc, copper, manganese, lead, thorium, and uranium; chlorides were used for tin and titanium, and ammonium molybdate, ammonium tungstate, and ammonium metavanadate for molybdenum, tungsten, and vanadium, respectively. All of the binary oxides contained molybdenum trioxide, tungsten trioxide, or triuranium octoxide as one component and one of the other above metal oxides as the other component. Aqueous solutions of the two salts (except chloride) were mixed and dried on a water bath, then decomposed to the oxide by heating in air at 300–400°C for 1 hr. The binary oxide powder so obtained was pressed into cylindrical shape (3 mm in diameter and 2 mm in length) and calcined at 550°C for five hr. When the starting material was chloride, it was first converted to hydroxide by precipitation from its aqueous solution of the other component. The hydroxide was filtered, washed with distilled water, and then mixed with an aqueuos solution of the other component. This mixture was dried, decomposed to oxide, tabletted, and calcined according to the same procedure as mentioned above.

RESULTS

1. Oxidation of Propylene over Various Transition Metal Oxides Combined with 10% (Metal Atom Basis) Molybdenum Trioxide

In the first paper of this series, the effect of catalyst composition on the reaction products was investigated in the oxidation of propylene over the Co_3O_4–MoO_3 binary system (*6*). Selective formation of acetone was found with the cobalt-rich catalysts (Co/Mo = 9/1 — 8/2).

We now report the catalytic activities of various other metal oxides containing 10 at. % molybdenum, namely, Fe_2O_3, TiO_2, SnO_2, Cr_2O_3, NiO, V_2O_5, ZnO, CuO, Mn_2O_3, ThO_2, and PbO_2. All runs were carried out under a constant GHSV, 660 ml-STP/ml-cat. hr, and fixed gas composition, propylene 20 vol %, oxygen 30%, steam 30%, nitrogen 20%, using 16.0–16.5 g of catalysts. The product distribution was determined over a range of temperature.

SnO_2–, TiO_2–, Fe_2O_3–, and Cr_2O_3–MoO_3 Catalysts

Selective oxidation of propylene to acetone was observed on these four catalysts, as with Co_3O_4–MoO_3. The results are shown in Table 1 and in Figs. 1, 2, and 3. The results on the SnO_2–MoO_3 catalyst was partly reported earlier (*7*, *8*). The most effective of these catalysts is SnO_2–MoO_3. The characteristics of this catalyst are found in its high activity and high selec-

TABLE 1
OXIDATION OF PROPYLENE OVER SnO_2–MoO_3[a]

Reaction temp (°C)	115	130	145	160	172	185	200
C'_3 conv (%)	1.9	4.1	8.2	12.4	14.3	18.0	20.7
Product (μmole/min)							
CH_3COCH_3	15.3	33.1	65.9	93.6	107.7	128.3	139.8
$CH_3CHOHCH_3$	2.7	2.9	2.9	2.7	2.2	1.7	1.3
(2/3) CH_3CHO	—	2.2	2.3	2.6	2.8	3.9	4.3
(2/3) CH_3COOH	—	—	1.1	2.4	3.1	5.0	6.8
(1/3) CO	—	—	—	1.4	1.5	5.1	7.3
(1/3) CO_2	—	0.2	5.4	11.1	17.2	24.9	35.4

[a] Catalyst, 17.2 g; GHSV, 660 ml-STP/ml-cat. hr; catalyst composition (Sn/Mo = 9/1).

tivity to acetone at the lowest reaction temperature. The catalyst is already active at 110–120°C where no other catalyst is active for acetone formation. The selectivity to acetone amounts to 80–85% of converted propylene below 172°C. The one-pass yield of acetone increases with increasing temperature until 200°C, but at higher temperatures the selectivity to acetone decreases to 70–75% of converted propylene on account of a considerable increase in carbon dioxide formation. Above 200°C, the product distribution could not be determined because of difficulty in temperature control caused by the exothermic reaction.

Some acetic acid and acetaldehyde were formed in the oxidation but acrolein, which is the main product of the allylic oxidation of propylene, could not be detected at any reaction temperature. A small amount of isopropyl alcohol, which is regarded as the reaction intermediate to acetone, was detected in the effluent gas in every case. The amount of isopropyl alcohol detected corresponds to 10–40% of the equilibrium concentration.

The second most effective catalyst is TiO_2–MoO_3. The results are shown in Fig. 1. This catalyst is also active for acetone formation at a reaction temperature as low as 110°C, but the rate of acetone formation is roughly one-third of that over SnO_2–MoO_3. It should be noted that a considerable amount of isopropyl alcohol is formed on this catalyst, especially at lower temperatures. The amount of isopropyl alcohol corresponds to approximately 50–60% of the equilibrium concentration at 125–145°C and approaches the equilibrium with increasing temperature. The selectivities to acetaldehyde and acetic acid are low and no acrolein is formed at any reaction temperature.

Fe_2O_3–MoO_3 is active for acetone formation at temperatures higher than 150°C. The results obtained at the temperature range of 150–300°C are shown in Fig. 2; the main product is acetone. The rate of acetone formation increases with increasing temperature to reach a maximum at 200°C, and then decreases as CO_2 and CO increase. The selectivity to acetone is roughly 80% of converted propylene below 200°C. The oxidation products, other than acetone and carbon oxides, are small amounts of acetic acid and acetaldehyde. No allylic oxidation products were detected under the conditions adopted for this work.

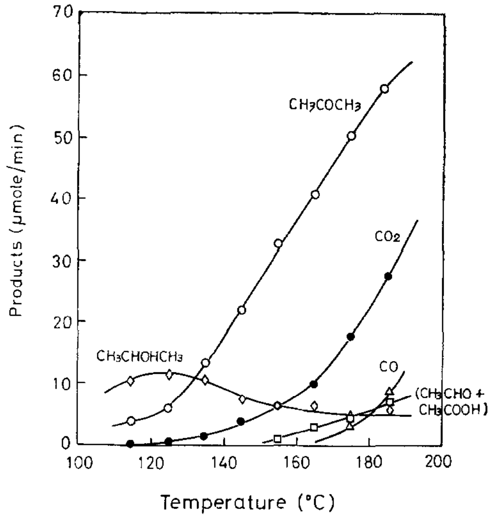

FIG. 1. Oxidation of propylene over TiO_2–MoO_3. Catalyst, 16.3 g; GHSV. 660 ml-STP/ml-cat. hr. Catalyst composition (Ti/Mo = 9/1).

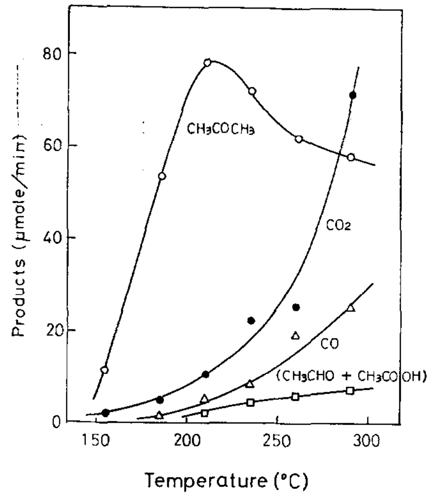

FIG. 2. Oxidation of propylene over Fe_2O_3–MoO_3. Catalyst, 16.2 g; GHSV, 660 ml-STP/ml-cat. hr. Catalyst composition (Fe/Mo = 9/1).

Cr_2O_3–MoO_3 is active above 200°C, as shown in Fig. 3. The oxidation on this catalyst is also selective. The main product is acetone and the by-products other than carbon oxides are acetaldehyde and acetic acid. The activity is approximately the same as that of Co_3O_4–MoO_3 reported previously (*6*).

V_2O_5–, NiO–, CuO–, and ZnO–MoO_3 Catalysts

These four catalysts are able to form acetone from propylene but with poorer selectivity. The results on V_2O_5–MoO_3 are shown in Fig. 4. A characteristic feature of this catalyst is the formation of large amounts of acetic acid at high temperatures. The selectivity to acetone amounts to 50% of converted propylene only below 200°C and when one-pass conversion of propylene is below 2%. The rate of acetone formation does not exceed 20 μmole/min, which is far lower than those obtained on the catalysts mentioned above. Small amounts (1–2 μmole/min) of acrolein are formed at higher reaction temperatures.

NiO–MoO_3 and CuO–MoO_3 are similar in their effectiveness. Typical runs are summarized in Table 2. Although some amounts of acetone are formed on these catalysts, the rate of formation does not exceed 10 μmole/min. The rates to acetic acid and acetaldehyde are fairly low on both catalysts. This is the characteristic difference from the V_2O_5–MoO_3 catalyst.

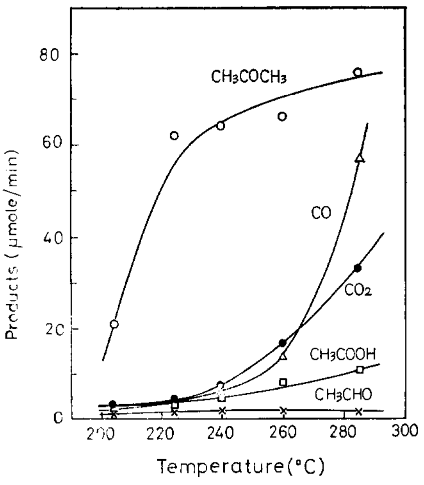

FIG. 3. Oxidation of propylene over Cr_2O_3–MoO_3. Catalyst, 16.2 g; GHSV, 660 ml-STP/ml-cat. hr. Catalyst composition (Cr/Mo = 9/1).

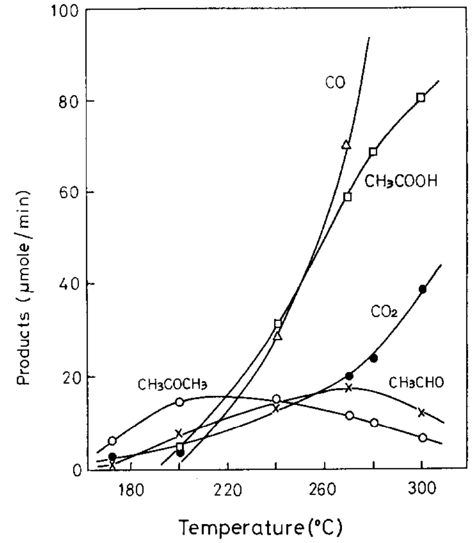

FIG. 4. Oxidation of propylene over V_2O_5–MoO_3. Catalyst, 16.3 g, GHSV; 660 ml-STP/ml-cat. hr. Catalyst composition (V/Mo = 9/1).

The catalytic activity of ZnO–MoO_3 is extremely low, as shown in Table 2. No oxidation is observed below 350°C under the conditions adopted in this work. Above 400°C, small amounts (3–4 μmole/min) of acetone are formed as well as acrolein, acetaldehyde, and large amounts of carbon oxides. Although acrolein formation increases with temperature, the increase in carbon oxides is far larger.

ThO_2–, PbO_2–, and Mn_2O_3–MoO_3 Catalysts

No oxygenated products other than carbon oxides were found in propylene oxidation over these three catalysts. The activities of ThO_2–MoO_3 and PbO_2–MoO_3 are extremely low. Propylene is not oxidized at all below 350°C. Most of the oxidized products above 350°C are carbon dioxide on PbO_2–MoO_3 and both carbon monoxide and dioxide on ThO_2–MoO_3. Mn_2O_3–MoO_3 is active above 200°C, forming only carbon dioxide.

TABLE 2

Product Distributions in the Oxidation of Propylene over NiO-, CuO-, and ZnO-MoO_3[a]

Catalyst	Reaction temp (°C)	C'_3 conv (%)	Product (μmole/min)					
			CH_3COCH_3	$CH_2{=}CHCHO$	(2/3)CH_3CHO	(2/3)CH_3COOH	(1/3)CO	(1/3)CO_2
NiO-MoO_3	271	1.84	8.58	—	0.82	2.64	Tr.	5.92
	295	3.27	5.94	2.14	1.42	2.66	9.20	10.4
	310	4.86	5.84	1.81	1.68	4.12	16.23	17.3
CuO-MoO_3	277	1.69	4.14	—	1.40	0.41	1.37	9.53
	300	4.43	8.65	—	1.76	0.93	2.55	30.13
ZnO-MoO_3	415	1.99	3.98	0.97	3.39	—	2.65	8.88
	442	3.68	2.99	2.29	5.31	—	7.53	18.7
	465	6.18	3.20	5.12	6.42	—	16.5	31.0
	485	8.90	3.61	11.7	8.67	—	23.7	41.9
	505	12.2	3.87	17.8	10.40	—	34.2	56.5

[a] Catalyst, 16 g; GHSV, 660 ml-STP/ml-cat. hr; catalyst composition (Ni, Cu, or Zn/Mo = 9/1).

2. Oxidation of Propylene over Molybdenum-Rich Catalysts

It is well known that allylic oxidation occurs over a number of molybdenum trioxide catalysts combined with minor amounts of other metal oxides. Thus, in the oxidation of propylene over molybdenum-rich Co_3O_4–MoO_3, the main oxidation products other than carbon oxides were acrolein and acrylic acid (*6*). Six other binary oxides, viz., SnO_2–, TiO_2–, Fe_2O_3–, V_2O_5–, NiO–, and CuO–MoO_3 of molybdenum-rich composition (70 at. % molybdenum) have now been examined. All runs were made using a flow system under a constant GHSV, 660 ml-STP/ml-cat. hr and at a fixed gas composition; propylene 6 vol %, oxygen 30%, nitrogen 34%, and steam 30%. The product distribution was determined over a range of temperature.

SnO_2-MoO_3 and TiO_2-MoO_3 Catalysts

The behaviors of SnO_2–MoO_3 and TiO_2–MoO_3 are little affected by the increase in molybdenum content. The results obtained on the SnO_2–MoO_3 catalyst (Sn/Mo = 3/7) are shown in Fig. 5. The characteristic features observed with low molybdenum SnO_2–MoO_3, i.e., the low temperature activity and the principal formation of acetone, are unchanged. The oxidation is highly selective below 180°C and the selectivity to acetone exceeds 80% of converted propylene.

Typical runs on molybdenum-rich TiO_2–MoO_3 catalyst are summarized in Table 3. The low-temperature activity and the principal formation of acetone in addition to substantial amounts of isopropyl alcohol are again observed with this molybdenum-rich catalyst. The amount of isopropyl alcohol corresponds to approximately 50–60% of the equilibrium concentration.

V_2O_5–, Fe_2O_3–, NiO–, and CuO-MoO_3 Catalysts

The results on the molybdenum-rich V_2O_5–MoO_3 catalyst are shown in Fig. 6. The increase in molybdenum content causes little change in catalytic behavior also in this case. Acetone is the main product at low temperatures. However, at high temperatures, large amounts of acetic acid are formed in addition to carbon oxides.

The behavior of Fe_2O_3–MoO_3 is strongly affected by its composition, as shown in Table 3. The molybdenum-rich Fe_2O_3–

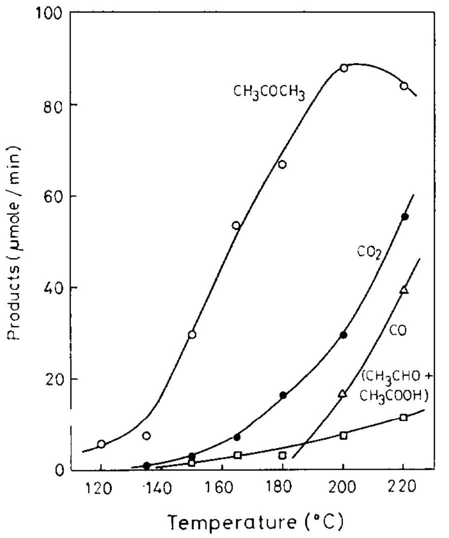

Fig. 5. Oxidation of propylene over molybdenum-rich SnO_2-MoO_3. Catalyst, 16.4 g; GHSV, 660 ml-STP/ml-cat. hr. Catalyst composition (V/Mo = 3/7).

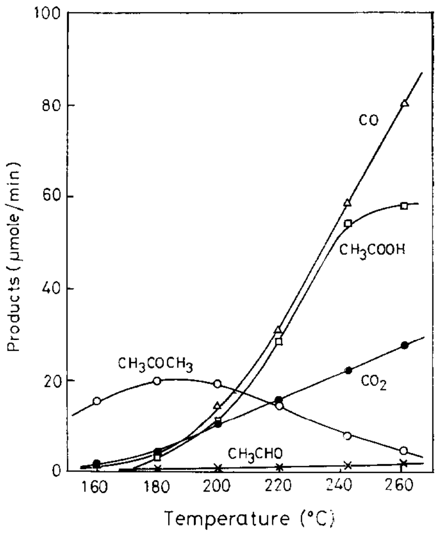

Fig. 6. Oxidation of propylene over molybdenum-rich V_2O_5-MoO_3. Catalyst, 16.3 g; GHSV, 660 ml-STP/ml-cat. hr. Catalyst composition (V/Mo = 3/7).

TABLE 3

PRODUCT DISTRIBUTIONS IN THE OXIDATION OF PROPYLENE OVER MOLYBDENUM-RICH TiO_2–, Fe_2O_3–, NiO–, AND CuO–MoO_3[a]

Catalyst	Reaction temp (°C)	C'_3 conv (%)	Product (μmole/min)						
			CH_3COCH_3	$CH_3CHOHCH_3$	$CH_2{=}CHCHO$	$(2/3)CH_3CHO$	$(2/3)CH_3COOH$	$(1/3)CO$	$(1/3)CO_2$
TiO_2–MoO_3	130	2.89	4.62	2.38	—	0.03	—	—	0.31
	145	6.17	12.2	1.88	—	0.07	—	—	1.52
	175	15.6	18.5	0.59	—	1.54	—	2.52	5.42
	190	21.2	20.8	0.56	—	2.07	1.36	3.58	11.3
	205	27.6	23.9	0.47	—	2.67	3.27	12.30	21.4
Fe_2O_3–MoO_3	255	1.87	0.53	0.07	—	0.12	1.16	—	3.03
	270	5.15	3.99	0.05	—	0.12	1.51	3.15	4.73
	300	8.48	1.50	0.02	0.04	0.07	2.36	10.30	8.01
	330	14.5	1.43	0.02	0.08	0.09	4.20	18.60	13.9
NiO–MoO_3	240	1.99	4.28	0.11	—	0.14	0.44	—	0.80
	280	5.27	8.63	0.06	0.08	1.13	0.48	1.26	3.64
	320	8.66	4.08	0.04	2.44	1.76	2.54	5.23	8.81
	360	21.4	2.38	Tr.	8.18	1.91	10.3	19.4	19.4
CuO–MoO_3	370	1.32	0.03	—	2.82	0.03	—	—	0.97
	420	2.24	0.04	—	4.35	0.05	—	—	2.09
	450	5.00	0.03	—	6.16	0.08	—	3.40	3.96
	480	10.4	0.03	—	9.81	0.14	—	8.26	9.95

[a] Catalyst, 16 g; GHSV, 660 ml-STP/ml-cat. hr; catalyst composition (Ti, Fe, Ni, or Cu/Mo = 3/7).

TABLE 4

PRODUCT DISTRIBUTIONS IN THE OXIDATION OF PROPYLENE OVER Co_3O_4–WO_3, SnO_2–WO_3, Co_3O_4–U_3O_8, AND SnO_2–U_3O_8[a]

Catalyst	Reaction temp (°C)	C'_3 conv (%)	Product (μmole/min)						
			CH_3COCH_3	$CH_3CHOHCH_3$	$CH_2{=}CHCHO$	$(2/3)CH_3CHO$	$(2/3)CH_3COOH$	$(1/3)CO$	$(1/3)CO_2$
Co_3O_4–WO_8	200	1.00	3.75	0.90	—	Tr.	—	—	5.27
	215	1.82	7.34	0.74	—	0.08	—	—	10.1
	230	3.91	1.88	1.35	—	0.20	—	—	35.2
SnO_2–WO_3	320	1.50	0.30	0.07	Tr.	0.06	0.08	4.60	9.91
	362	6.10	0.18	Tr.	3.72	0.14	0.12	18.2	36.8
	380	11.20	0.35	—	7.20	0.25	1.64	35.7	63.6
	400	19.30	6.50	—	8.55	1.68	1.40	57.3	113.3
	422	27.70	6.08	—	16.5	3.17	1.17	84.3	159.2
Co_3O_4–U_3O_8	230	0.60	1.30	Tr.	—	Tr.	—	—	4.71
	255	1.68	Tr.	Tr.	—	Tr.	—	—	17.0
	290	6.39	0.02	Tr.	—	Tr.	—	—	64.7
SnO_2–U_3O_8	220	0.55	Tr.	0.03	—	Tr.	—	0.69	4.54
	240	4.09	0.03	0.05	—	0.05	—	11.0	28.3

[a] Catalyst, 16 g; GHSV, 660 ml-STP/ml-cat. hr.

MoO_3 catalyst is no longer effective for acetone formation. Although small amounts of acetone, acrolein, acetaldehyde, and acetic acid are formed, propylene is mostly oxidized to carbon oxides.

The oxidation over the molybdenum-rich NiO–MoO_3 catalyst is not so selective, as shown in Table 3. Acetone is the main product at 240 or 280°C but the selectivity decreases at higher temperatures. Considerable amounts of acrolein and acetic acid are formed at 360°C in addition to carbon oxides.

Acrolein is the main product in the oxidation over the molybdenum-rich CuO–MoO_3 catalyst. The results are also listed in Table 3. The catalytic activity of CuO–MoO_3 is decreased very much by the increase in molybdenum concentration, as in the case of Co_3O_4–MoO_3 (*6*). The reaction product over both binary oxides changes from acetone to the allylic oxidation products according to the catalyst composition.

3. Oxidation of Propylene over SnO_2 and Co_3O_4 Combined with WO_3 or U_3O_8

It is well known that tungsten oxide and uranium oxide resemble molybdenum trioxide in their effect as heterogeneous oxidation catalysts for olefins (*2, 9–11*). In the present work, WO_3 and U_3O_8 have been examined for their activity in the oxidation of propylene to acetone by combining with tin oxide or cobalt oxide, the oxides which were most effective in the molybdenum trioxide series. All the binary oxides tested were composed of nine parts of tin or cobalt and one part of tungsten or uranium on an atom basis. The runs were carried out under the same conditions as described in Section 1. The product distributions are summarized in Table 4. As can be seen in Table 4, no catalyst is particularly effective for acetone formation. The selectivity to acetone is fairly high on Co_3O_4–WO_3 catalyst only when the conversion of propylene is below 2%. However, the selectivity to acetone decreases markedly with increasing temperature. At 230°C, most of the reacted propylene is converted to carbon dioxide at a propylene conversion of 3.91%. The catalytic activity of SnO_2–WO_3 is far lower than that of SnO_2–MoO_3 and propylene is not oxidized at temperatures below 300°C; above 300°C carbon oxides are the predominant products.

The catalytic activity of SnO_2– or Co_3O_4–U_3O_8 to form acetone is even poorer than those combined with WO_3. Oxidation products other than carbon oxides only occur in trace amounts.

DISCUSSION

The results obtained in this work can be summarized as follows;

1. Acetone formation is not limited to a specific catalyst, but several transition metal oxides combined with molybdenum trioxide are active for this oxidation. The effective catalysts are TiO_3–, Fe_2O_3–, and Cr_2O_3–MoO_3, as well as Co_3O_4–MoO_3 and SnO_2–MoO_3 reported previously (*6, 7*).
2. Molybdenum trioxide is an essential component for an effective catalyst. Tungsten trioxide or triuranium octoxide fails to be an effective component instead of molybdenum trioxide.
3. Over any effective catalyst, the reaction temperature to form acetone is much lower than that of allylic oxidation. No allylic oxidation product is formed under the reaction conditions of acetone formation.
4. Generally speaking, a molybdenum-poor composition is favorable for acetone formation. However, in the cases of SnO_2–MoO_3 and TiO_2–MoO_3, the selective formation of acetone is observed independently of their composition.

In a previous paper (*8*), we proposed that ketone is produced via hydration of the olefin to form an alcoholic intermediate, followed by oxydehydrogenation. In accordance with this mechanism small amounts of isopropyl alcohol were detected in several runs, especially those at low temperatures. The fact that the reaction temperature to form acetone is much lower than that of the allylic oxidation over any binary oxide seems to support the proposed mechanism via hydration. This fact can be easily understood according to the mechanism, since the equilibrium constant of the hydration is favorable for alcohol at low temperatures and alcohol is rapidly oxidized to the corresponding ketone on an active catalyst (*8*).

Some of the molybdenum-rich binary oxides, such as SnO_2–MoO_3 and Fe_2O_3–MoO_3, have been reported as allylic oxidation catalysts (*2*). However, a substantial formation of acrolein or acrylic acid was not observed in this work. This discrepancy is mainly due to the low reaction temperature adopted in this work. The fairly high surface area of the catalysts, e.g., 16.4 and 21.0 m^2/g for SnO_2– and TiO_2–MoO_3, respectively, and the fairly low GHSV adopted in this study, e.g., 660 ml-STP/ml-cat. hr, may have some role in the acetone formation observed at low temperatures.

It is important to try to understand what is the essential factor in those catalysts effective for acetone formation. It seems that molybdenum trioxide is an indispensable component. However, it is difficult to find something common to those second components in the effective catalysts. Neither the chemical properties of the element involved in the effective oxide, e.g., position in the periodic table, valency, electronegativity, and atomic radius, nor the catalytic activity and the chemical reactivity of the second oxide itself (*12–14*) can give a criterion for an effective oxide.

According to the mechanism of acetone formation proposed in our previous paper (*8*), propylene is hydrated to an alcoholic intermediate in the rate-determining step followed by oxidative dehydrogenation to acetone. It is reasonable in this mechanism that the first hydration step should be promoted by an acid site of the catalyst. The relatively lower reaction temperature in the acetone formation is understandable as an acid-catalyzed reaction. Thus the essential nature of the effective catalyst seems to be related to creation of an acid site by the combination of the two oxides. This will be studied in a forthcoming paper.

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REFERENCES

1. Smidt, J., Hafner, W., Jira, R., Sedlmeier, J., Sieber, R., Ruttinger, R., and Kojer, H., *Angew. Chem.* **71**, 176 (1959); Smidt, J., Hafner, W., Jira, R., Sieber, R., Sedlmeier, J., and Sabel, A., *Angew. Chem.* **74**, 93 (1962).

2. Sampson, R. J., and Shooter, D., "Oxidation and Combustion Reviews" (C. F. H. Tipper, ed.), Vol. 1, p. 223. Elsevier, 1965.

3. Adams, C. R., and Voge, H. H., *Advan. Catal. Relat. Subj.* **17**, 151 (1967).

4. Simons, Th. G. J., Verheijen, E. J. M., Batist, Ph. A., and Schuit, G. C. A., "International Oxidation Symposium," II–29. San Francisco, 1967.

5. Buiten, J., *J. Catal.* **10**, 188 (1968).

6. Moro-oka, Y., Tan, S., and Ozaki, A., *J. Catal.* **12**, 291 (1968).

7. Moro-oka, Y., Takita, Y., Tan, S., and Ozaki, A., *Bull. Chem. Soc. Jap.* **41**, 2820 (1968).

8. Tan, S., Moro-oka, Y., and Ozaki, A., *J. Catal.* **17**, 132 (1970).

9. Margolis, L. Ya., *Advan. Catal. Relat. Subj.* **14**, 429 (1963).

10. Sachtler, W. M. H., and de Boer, N. H., *Proc. Int. Congr. Catal., 3rd 1964*, **1**, 252 (1965).

11. Grasselli, R. K., and Callahan, J. L., *J. Catal.* **14**, 93 (1969).

12. Boreskov, G. K., *Advan. Catal. Relat. Subj.* **15**, 286 (1964).

13. Moro-oka, Y., and Ozaki, A., *J. Catal.* **5**, 116 (1966).

14. Moro-oka, Y., Morikawa, Y., and Ozaki, A., *J. Catal.* **7**, 23 (1967).