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NOTE

Propane Oxydehydrogenation over Metal Tungstates

Metal tungstates containing Ni, Co, Zn, Fe, and Ce, and the binary system $Ni_{0.5}Co_{0.5}WO_4$, were investigated for the oxydehydrogenation of propane. It was found that the tungstates, in particular $CoWO_4$, constitute a new class of catalysts holding some promise for paraffin oxydehydrogenation, in addition to the previously studied systems based on vanadium-containing compounds (1) and on nickel–cobalt–molybdates (2).

There exists a striking difference between the now studied tungstates and the earlier studied molybdates, with $CoWO_4$ being the most effective system among the tungstates (8% propylene yield at 20% conversion), while in molybdates $NiMoO_4$ is most effective (10% propylene yield at 40% conversion). This observed, structure dependent Co for Ni switch was unexpected.

The catalyst preparation, characterization, and evaluation was performed in an manner analogous to that described earlier (2), using the same instruments and catalytic units. The source of tungsten for the preparation of the tungstates was ammonium meta tungstate. Conversion, selectivity, and yield are defined as reported earlier (2), and carbon, hydrogen, and oxygen closures were typically better than 95%.

Metal tungstates prepared and evaluated in this study include $NiWO_4$, $CoWO_4$, $ZnWO_4$, $Fe_2W_3O_{12}$, and $Ce_2W_3O_{12}$ and the binary tungstate $Ni_{0.5}Co_{0.5}WO_4$. All catalysts were supported on SiO_2 (80 wt% active component/20 wt% support).

X-ray diffraction patterns of the catalysts are typical of the respective compounds, some indicating the presence of multiple phases. The diffraction pattern of the $Ce_2W_3O_{12}$ composition resembles strongly that of $Ce_4W_9O_{33}$ (JCPDS-ICDD 25-1921) with the major three diffraction lines and their respective relative intensities at: 3.474(100), 3.167(54), 3.59(36), indicating that not all of the Ce had combined with the W-oxide. The $Fe_2W_3O_{12}$ pattern indexes well with its tetragonal structure (JCPDS-ICDD 24-538, 3.369(100), 3.545(45), 3.762(26)). Some presence of WO_3 and $FeWO_4$ is also indicated. The $ZnWO_4$ is typical of its monoclinic phase (JCPDS-ICDD 15-774, 2.933(100), 2.907(84), 3.733(44)). The $NiWO_4$ and $CoWO_4$ are both monoclinic and show the classical X-ray patterns of the two structures, respectively. The $Ni_{0.5}Co_{0.5}WO_4$ pattern is typical of a solid solution between $NiWO_4$ and $CoWO_4$ and shows the expected lattice expansion from Ni– to Co–tungstate. For example, the strongest line of $Ni_{0.5}Co_{0.5}WO_4$ at $d = 2.895$ Å belonging to the (111) reflection lies almost exactly halfway between the (111) reflection of $NiWO_4$ ($d = 2.888$) and $CoWO_4$ ($d = 2.914$).

Salient physical data and catalytic results are summarized in Tables 1 and 2. The surface areas are similar for all catalysts, ranging from 20 to 31 m^2/g (Table 1), consistent with the silica support providing most of the porosity and surface area of these catalysts.

Propylene selectivities at 7 and 15% propane conversion and first order rate constants for propane disappearance are summarized in Table 1. Selectivities to non-CO_x products (mainly propylene) as a function of propane conversion (Fig. 1) display the typical behavior of selectivity decline with an increase in conversion. $CoWO_4$ emerges as the most efficient system among the investigated tungstates. At low conversion, reasonable first order kinetics are indicated for the conversion of propane to propylene, at higher conversions, some of the compositions display a kinetic behavior more complex than first order.

The activity ordering for propane conversion based on the relative first order constants is:

$$k_{\mathrm{rel}}\mathrm{Co}(100) \sim \mathrm{Fe}(98) > \mathrm{NiCo}(22) > \mathrm{Ni}(16) > \mathrm{Ce}(12) \sim \mathrm{Zn}(9).$$

Since the surface areas of these tungstates are very similar, the activity ratings do not change when surface area corrections are also taken into account (Tables 1 and 2).

In another set of experiments (Table 2), the above catalysts were evaluated at a single condition (560°C, 9 cc C_3°/9 cc O_2/42 cc N_2 feed over 1 g catalyst), giving an activity ordering essentially the same as that above, with Co–tungstate being the most active catalyst and Zn–tungstate the least active.

The $CoWO_4$ catalyst was also evaluated at three different temperatures (500, 530, and 560°C) giving a propane activation energy, E_a, of 14.2 kcal/mole. This value is considerably lower than that obtained for $Ni_{0.5}Co_{0.5}MO_4$ ($E_a =$ 21.5 kcal/mole), and is consistent with the possibility that Co might reside in its high spin state in the tungstate structure, while it is in its low spin state in the molybdate structure. The radical character of the $(\mathrm{Co{-}O\cdot})$ moieties in the tungstate framework might provide for the paraffin activating centers.

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TABLE 1

Summary of Catalytic Data for Propane Oxidation over Metal Tungstates

		Selectivity to useful products			
Catalyst	Surface area (m^2/g)	at 7% C_3° conversion	at 15% C_3° conversion	k ($s^{-1} \times 10^{-3}$)	k/SA ($\times 10^{-3}$)
$CoWO_4$	23	57.0	48.6	132	5.74
$NiWO_4$	31	22.9	—	21	0.7
$Ni_{0.5}Co_{0.5}WO_4$	26	—	30.9	29	1.11
$Fe_2W_3O_{12}$	24	19.2	10.0	130	5.42
$Ce_2W_3O_{12}$	20	25.0	10.2	16	0.80
$ZnWO_4$	28	28.2	—	9	0.32
Quartz-packed reactor	—	—	—	4	—

Note. Conditions: $C_3^\circ/O_2/N_2$ feed (15/15/70 feed ratio), WHSV varied to achieve a wide range of C_3° conversions, 560°C, 1 atm total pressure.

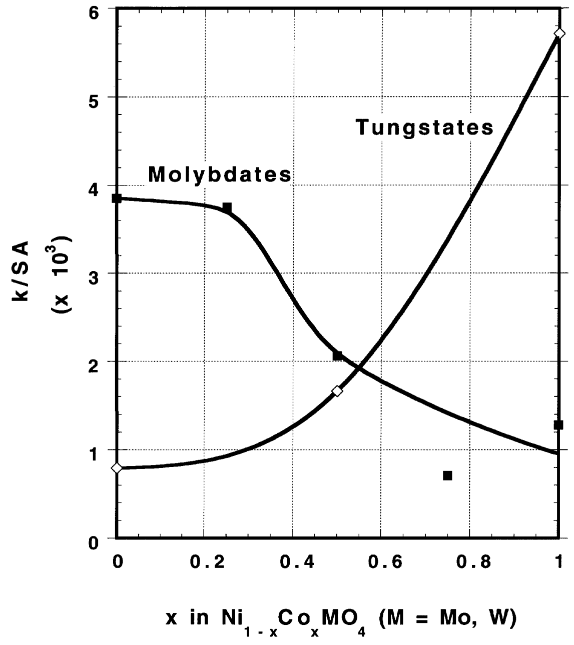

FIG. 2. Surface area normalized rate constants vs X for $Ni_{1-x}Co_xMO_4$ (M = Mo, W).

A remarkable observation of the current study, comparing the catalytic properties of metal tungstates with those of the earlier studied corresponding molybdates (2), is that Co and Ni switch positions as the respectively most active paraffin activating components in their respective catalyst classes. Thus, $CoWO_4$ is the most active composition among the tungstates, while $NiMoO_4$ is most active among the molybdates. A plot of k/SA versus composition $Ni_{1-x}Co_xMO_4$, where $M =$ Mo or W, illustrates this point (Fig. 2). This observation is also consistent with our above-mentioned conjecture of the difference in the spin states of the cobalt. The conjecture presumes that the cobalt lies in a high spin state in the tungstate, while it is in a low spin state in the molybdate. This is consistent with cobalt forming an inorganic radical (Co–O·) in the tungstate and not in the

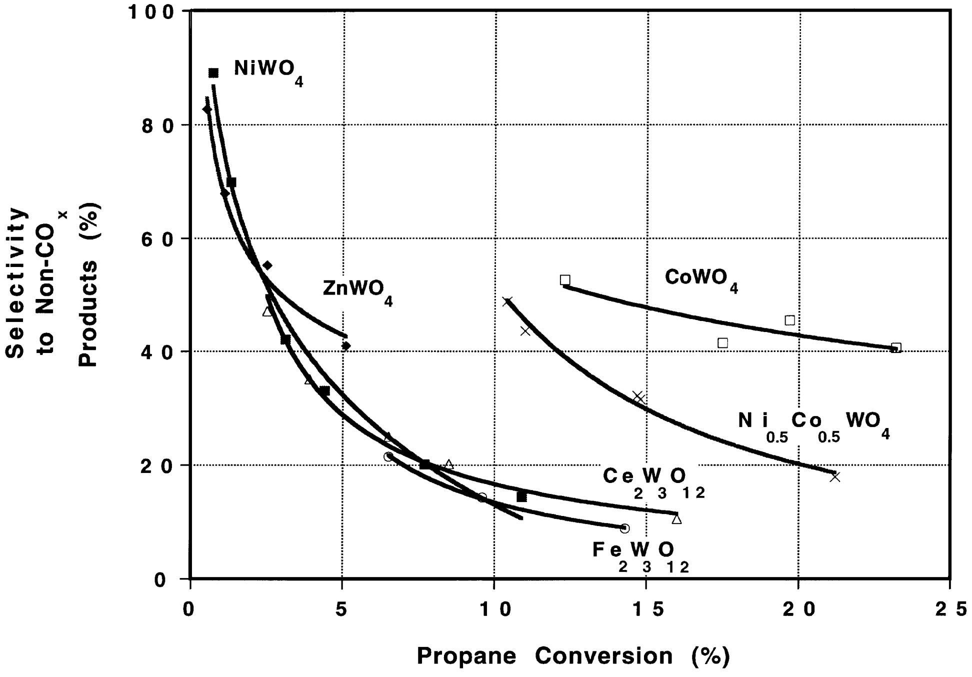

FIG. 1. Propane oxidation over metal tungstates.

TABLE 2

Summary of Catalytic Data for Propane Oxidation over Metal Tungstate and Molybdate Catalysts

Catalyst	C_3° conversion	Non-CO_x selectivity	Yield	$C_{3=}$ Selectivity	Acrolein selectivity	Surface area	O_2 conversion	k $(s^{-1} \times 10^{-3})$	k/SA
$CoWO_4$	23.1	39.3	9.1	39.0	0.3	23	81.0	131	5.71
$NiWO_4$	4.8	38.6	1.9	32.9	5.8	31	15.7	24.6	0.79
$Ni_{0.5}Co_{0.5}WO_4$	10.4	44.0	4.6	41.8	2.2	33	31.0	54.9	1.66
$Fe_2W_3O_{12}$	18.2	9.5	1.8	9.0	0.5	43	78.4	100	2.3
$ZnWO_4$	1.5	65.1	0.9	62.2	3.0	28	2.8	7.6	0.27
$Ce_2W_3O_{12}$	5.9	33.2	1.9	32.4	0.8	20	5.9	30.4	1.52
$CoWO_4$ (530°C)	17.6	44.3	7.8	44.0	0.3	23	57.2	96.7	4.21
$CoWO_4$ (500°C)	12.6	50.5	6.4	38.5	0.2	23	38.5	67.3	2.93
$NiMoO_4$	26.6	64.0	17.0	60.4	3.6	40	60.8	154	3.85
$CoMoO_4$	4.4	70.0	3.1	65.4	4.6	18	8.4	23	1.28
$Ni_{0.5}Co_{0.5}MoO_4$	12.1	75.8	9.2	71.4	4.4	31	20.3	64	2.06

Note. Conditions: 560°C except as indicated, 1 atm. Feed (in cc/min): 9 $C_3^\circ/9O_2/42\ N_2$ over 1 g catalyst.

molybdate, a species highly active in attacking a paraffin in its rate limiting step of a methylene hydrogen abstraction. In this manner it is similar to the inorganic radical ($V{-}O\cdot$ or $V^{4+}{=}O$) contained in V-based paraffin activating catalysts (3). Consistent herewith is also the similarity of the catalytic behavior of Co–tungstate and V−Mg-oxide (1) in the oxydehydrogenation of propane.

We attempted to resolve more fully the question of the cobalt spin states by measuring the magnetic susceptibility of the respective Co–tungstates and Co–molybdates. However, we were unable to make any unambigeous conclusions. Additional spectroscopic (ESR) work is needed, as well as molecular orbital calculations, to further elucidate this unexpected finding of the structure dependent Co for Ni (tungstates) and Ni for Co (molybdates) activity switches.

In summary, metal tungstates such as $CoMoO_4$ constitute a new class of paraffin oxydehydrogenation catalysts. Their catalytic behavior is similar to that of V−Mg-based catalysts (1) and is somewhat inferior to the Ni−Co–molybdate systems (2). An interesting comparative observation is that in the $Ni_{1-x}Co_xWO_4$ system, $CoWO_4$ is the best propane oxydehydrogenation catalyst, while in the $Ni_{1-x}Co_xMoO_4$ system it is $NiMoO_4$. A possible explanation of this unexpected behavior may lie in the difference of the cobalt electron spin states as a function of catalyst structure. Additional work is needed to further elucidate our conjectures and herewith contribute to the development of improved paraffin activating catalysts.

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