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Oxidative Dehydrogenation of Propane on Supported Molybdena Catalysts: Effect of the Support Nature and of Additives

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Oxidative dehydrogenation of propane has been studied on molybdena deposited on SiO_2, Al_2O_3, TiO_2, and MgO. The catalytic performance depended on the support nature, the selectivity to propene at iso-conversion decreasing in the sequence: $MoO_x/SiO_2 > MoO_x/Al_2O_3 \sim MoO_x/TiO_2 > MoO_x/MgO$. Introduction of the K, Cr, Ni and V additives to MoO_x/SiO_2 and Cr to MoO_x/MgO catalysts led to the increase of the total activity. The increase of the selectivity to propene was observed for the Cr and Ni additives, whereas the K and V in the MoO_x/SiO_2 catalysts decreased the selectivity (K and higher amounts of V), or did not affect it (lower amounts of vanadium).

Key words: supported molybdena catalysts; additives, propane oxidative dehydrogenation

The oxide systems found promising for oxidative dehydrogenation, ODH of lower alkanes – a reaction of great recent interest as a favourable alternative to classical dehydrogenation for production of olefins – contain usually vanadium and molybdenum [1–4]. Among the molybdenum-based systems, nickel and cobalt molybdates give the best selectivities (65–80% at 10% conversion) and yields (8–12%) of olefins in ODH of propane at temperatures > 500°C [5–7]. Good performance of Mg molybdates in ODH of propane was also reported, though the activity in this system has been ascribed to a layer of excess MoO_x present on the molybdates surface [8,9]. The excess of Mo in Ni–Mo–O catalysts has enhanced activity and selectivity in the propene ODH [7]. Molybdena dispersed on oxide supports, such as TiO_2 [10,11], Nb_2O_5, ZrO_2, SiO_2, Al_2O_3 and MgO [12], and ZrO_2 [13] has been also tested in ODH of propane, giving results comparable to those obtained for the molybdates. The catalytic properties of oxide catalysts can be improved by introduction of small amount of additives into a catalyst [14]. For the ODH reactions of lower alkanes alkali metal additives have been found to improve the selectivity to propene in the ODH of propane on V_2O_5/TiO_2, MoO_3/TiO_2 [10,11], V_2O_5/Al_2O_3 [15], V_2O_5/SiO_2 [16] and MoO_3/MgO-γ-Al_2O_3 [17] catalysts, the effect being explained by modification of acid-base properties of the catalysts by alkalis. Little is known about the effect of other additives, in particular of transition metal ions, which can modify other – beside acido-basic – properties, such as charge transfer in the solid and redox potential of the active V or Mo centres, M–O bond strength on the surface or in the bulk of oxide catalysts, and the type of surface oxygen species. Ample literature reviewed in [14] shows that all these properties may control both activity and selectivity in oxidation reactions. Among non-alkali, the Fe, Cr, and V additives were found to increase the overall activity of mixed nickel-cobalt molybdates in the propane-oxygen reactions, with the considerable decrease, however, in the selectivity to propene [6]. On the other hand, the Re additive increased the selectivity to propene in the same reaction on MoO_3/TiO_2 catalysts [18].

In this work the catalytic performance in ODH of propane has been studied for molybdena supported on oxides of different nature (acidic SiO_2, basic MgO and amphoteric Al_2O_3, TiO_2). In contrast to [12], in which the authors used the same weight % of the molybdena phase on supports of very different surface area, the catalysts prepared in this work contained the same surface concentration of the active molybdena. For some of the catalysts, the effect of the addition of K, Cr and Ni has been also examined. For the MoO_3/SiO_2 catalyst, (which turned out in preliminary experiments the most promising system), the effect of the addition of vanadia (another active component of the propane ODH catalysts) on catalytic performance in the title reaction was also tested.

EXPERIMENTAL

Preparation of the catalysts: The catalysts were obtained by impregnation of commercial supports with aqueous solution of ammonium paramolybdate, evaporation, drying at 120°C for 5 h and calcination for 5 h at 500°C in a stream of air. The additives were introduced by adding appropriate amounts of solutions of nitrates of K, Cr, and Ni to the ammonium paramolybdate solution. The surface loading of the molybdena phase was the same for all the catalysts and corresponded to 2 theoretical monolayers, mnl of MoO_3: 1 mnl estimated from the crystallographic data of MoO_3 contained 6.5 at Mo/nm^2 of the support surface. The Mo content of 2.4 mnl was suggested in [12] as optimal for the TiO_2 support. The additive A/Mo ratio was 0.2 for the Cr and Ni and 0.1 for the K additive. In the further text the catalysts were described by a symbol AMoX, where A denotes an additive, X a cation of the oxide support. Table 1 gives a list of the catalysts, the origin, and specific surface area of the supports obtained with the BET method. The specific area of the catalysts checked for selected samples (MoO_3/TiO_2) were close (within 10%) to those of the supports.Two MoSi preparations with the addition of vanadia were prepared using for impregnation a mixture of the ammonium paramolybdate and metavanadate solutions. The content of molybdena and vanadia phases corresponded to 1 mnl MoO_3–0.5 mnl V_2O_5 (atomic ratio Mo/V = 1.3) [sample K1Mo0.5V], and 0.75 mnl MoO_3–1.5 mnl V_2O_5 (Mo/V = 0.33) [sample K0.75Mo1.5V]. Since pure vanadia dispersed on SiO_2 was found little selective in the ODH of propane [16], small amounts of potassium (K/V+Mo = 0.05) were also introduced to these two preparations to suppress the expected total combustion on the vanadia phase.

Catalytic activity measurements: The activity of the catalysts in oxidative dehydrogenation of propane was measured in a fixed bed flow apparatus between 360–520°C. A stainless steel reactor (120 mm long, internal diameter 13 mm) was coupled directly to a series of gas chromatographs. Propene and carbon oxides (CO and CO_2) were found to be the main reaction products.The amounts of the degradation, C_2 products and of oxygenates (acrolein and acrylic acids) were below 1% of the total amount of products. The reaction mixture contained 7.1 vol.% of propane in air. 0.5 ml of a catalyst sample of grain size 0.63–1 mm, diluted with quartz beads was used. The composition of the reaction mixture was controlled with mass flowmeters. Since the selectivity to propene decreased with the increasing conversion

Table 1. List of samples of MoO_x/oxide support catalysts.

Symbol	Support		wt %	
	Origin	Sp. surface area $[m^2/g]$	Mo	Additive
$MoAl_n$	MERCK(neutral)	159	24.28	–
$MoAl_b$	MERCK(basic)	111	18.29	–
$MoTi_{13}$	Tioxide LTD, batch: NP 93/203	13	3.32	–
$MoTi_{48}$	Tioxide LTD, batch: NP 93/204	48	8.82	–
MoMg	UBICHEM	72	12.70	–
MoSi	Aerosil 200	175	26.10	–
KMoSi	Aerosil 200		23.60	0.96
CrMoSi	Aerosil 200		25.40	2.76
NiMoSi	Aerosil 200		25.30	3.10
K1Mo0.5VSi	Aerosil 200		14.04	0.50 (K) 5.1 (V)
K0.75Mo1.5VSi	Aerosil 200		9.70	0.82 (K) 16.3 (V)
CrMoMg	UBICHEM	72	12.57	1.37

(a typical behaviour for the ODH reactions on oxide catalysts [1–4]), the selectivities at iso-conversions were compared. To obtain the same conversions for a series of catalysts of different activities, the total flow of the reaction mixture at a given reaction temperature varied between 20–120 ml/min, which corresponded to the contact time τ = 0.2–1.5 s. On the other hand, the flow rate (contact time) had to be adjusted for some catalysts to keep the conversions below ~20%: above these values the conversions were limited by the high consumption of oxygen. The carbon balance for conversions higher than about 10% was better than 97 ± 2%. At lower conversions the balance was poorer and hence the selectivities to different products were calculated from the formula: $S_i = c_i / \sum c_i$ where c_i are concentrations of products i. The total conversion X_p was calculated as:

$$X_p = \frac{c_p^0 - c_p}{c_p^0}$$

where c_p^0 and c_p are the concentrations of propane at the inlet and outlet of the reactor respectively. The pure supports were not active in the studied conditions; the total propane conversion not exceeding 1% at 500°C.

RESULTS AND DISCUSSION

Effect of the support nature: The activity and selectivity of the catalysts in the ODH of propane depended on the type of the oxide support. Table 2 compares temperature of 5% conversion T_5, taken as a measure of the activity, and selectivity to propene at this conversion for the series of MoO_3/oxide support catalysts without additives. Molybdena dispersed on alumina appears to be the most active catalyst (the lowest T_5), whereas the lowest activity is shown by molybdena on SiO_2.

Table 2. Activity* and selectivity to propene in oxidative dehydrogenation of propane on MoO_x/oxide support catalysts.

Catalyst	T_5, [°C]	Selectivity to propene, S_5^{**}, [%]
$MoAl_n$	360	52
$MoAl_b$	360	59
$MoTi_{48}$	430	52
$MoTi_{13}$	460	57
MoMg	500	41
MoSi	520	70

* Temperature of 5% propane conversion T_5, taken as a measure of the activity, $\tau = 1.5$ s.
** S_5 – selectivity at 5% conversion.

For catalysts containing supports of the same nature, but of different provenance and different surface area, some differences in the activity (MoTi catalysts) and selectivity to propene (MoTi, MoAl samples) can be observed: the catalysts of lower specific surface area being more selective. On the whole, the deposition of molybdena on acidic support (SiO_2) leads to the most selective catalyst, the basic support gives the least selective catalyst (MoMg), whereas the selectivities of the catalysts containing alumina or titania supports are similar. The sequence of the selectivities and their values are different than those reported in [12], which can be due to the different molybdena loading and different origin of the support. It can be, however, observed that, similarly like in [12], the molybdena on silica is the most selective though the least active catalyst.

For the most active MoAl catalysts, for which measurable conversion was obtained at relatively low temperatures of ~350°C, the variations of the conversion and selectivities to various reaction products at the same contact time (1.5 s) with the reaction temperature are shown in Fig. 1. The increase in the conversion with the temperature is accompanied by a decrease in the selectivity to propene and increase in

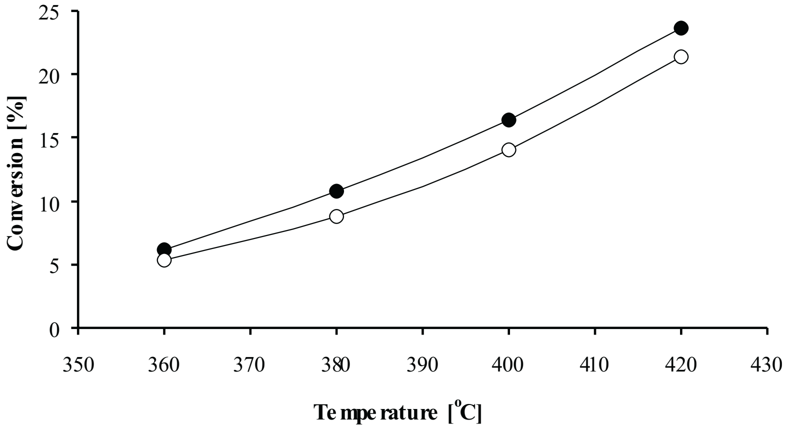

Figure 1. Changes of the propane conversion (at $\tau = 1.5$ s) with the reaction temperature for MoO_3/Al_2O_3 catalysts. Black circles: $MoAl_n$, open circles: $MoAl_b$ catalyst.

the selectivity to undesirable carbon oxides. CO formation is favoured over CO_2, the CO/CO_2 ratio being ~2. For the same catalysts at a constant reaction temperature of 400°C, the selectivity to propene decreases and that to CO_x increases with the increase in the conversion (Fig. 2). The variations of the conversion (from ~4 – 20%) are induced by variations of the contact time (from 0.25 to 1.5 s). The changes in the selectivity with the conversion observed on changing both the reaction temperature and the contact time (at constant temperature) follow a common trend in the ODH reactions on oxide catalysts [1–4,19], indicating a consecutive character of the reaction: propene formed in the first step of the reaction is further oxidized to undesirable carbon oxides.

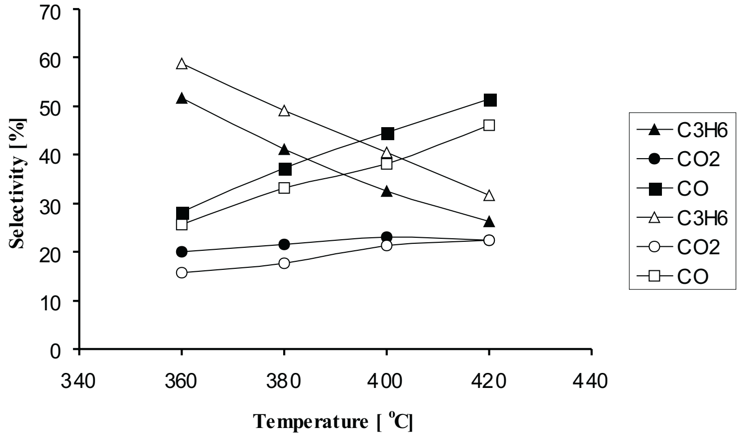

Figure 2. Changes of the selectivity to various products in propane-oxygen reactions (at $\tau = 1.5$ s) with the reaction temperature for MoO_3/Al_2O_3 catalysts. Black symbols: $MoAl_n$, white symbols: $MoAl_b$ catalyst.

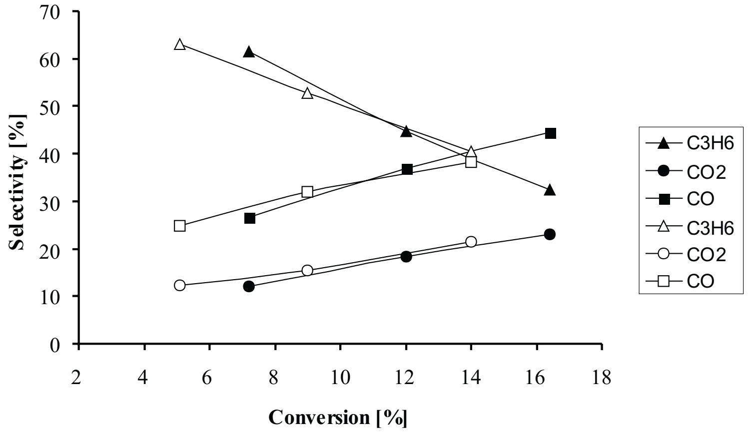

Figure 3. Selectivity to various products as a function of the propane conversion for MoO_3/Al_2O_3 catalysts. Reaction temperature: 400°C. Black symbols: $MoAl_n$, white symbols: $MoAl_b$ catalyst.

The differences in activity and selectivity of the catalysts of the same Mo content, but dispersed on different supports, presented in Table 2, suggest a different type of dispersion of the active molybdena phase. Further studies on characterization of the catalysts are necessary to determine the structure of the molybdena phase in each case. On the basis of the literature data on the structure of dispersed molybdena [21], one may envisage formation of bidimensional MoO_x species (mono- and polymeric), bound to a support, and bulk MoO_3 depending on the support nature. By analogy with the supported vanadia catalysts [22,23], each of these species may be characterized by different redox and acido basic properties, which, in turn, should affect the catalytic performance [14].

Effect of the additives: Table 3 presents conversions of propane and selectivities to propene at conversions 3 and 6% for reaction temperatures 500 and 520°C for MoSi catalysts with K, Cr and Ni additives. Table 4 gives similar data for MoMg catalysts with the Cr additive: in view of the higher activities (conversions) of this system, it was possible to compare the selectivities at slightly higher conversions of 5 and 8%. For the MoSi catalysts introduction of all the additives leads to the increase in the propane conversion for both reaction temperatures. Cr and Ni additives give increase in the selectivity, whereas the K additive leads to a decrease. For the MoMg catalysts, the Cr additive increases the conversion and the selectivity. The yields of propene of ~10% obtained for NiMoSi and CrMoMg catalysts are close to those reported in the literature for the best systems, and show that introduction of the transition metal additives may be an effective way to ammeliorate catalytic performance of molybdate-based catalysts in the ODH of propane.

Table 3. Effect of additives to MoO_3/SiO_2 catalyst on catalytic properties in oxidative dehydrogenation of propane.

Catalyst	Conversion* [%]		Selectivity C_3H_6 [%]	
	Temperature [^oC]		S_3	S_6
			Temperature [^oC]	
	500	520	500	520
MoSi	1.5	3.1	–	~70
KMoSi	2.7	5.4	64	60
CrMoSi	4.0	7.6	68	74
NiMoSi	8.4	13.6	79	75

S_x – selectivity at propane conversion x,
* τ = 1.5 s.

Table 4. Effect of Cr additive to MoO_3/MgO catalyst on catalytic properties in oxidative dehydrogenation of propane.

Catalyst	Conversion* [%]		Selectivity C_3H_6 [%]	
	Temperature [°C]		S_3	S_6
			Temperature [°C]	
	500	520	500	520
MoMg	4.6	4.0	41	49
CrMoMg	12.0	19.5	52	56

S_x – selectivity at propane conversion x,
* τ = 1.5 s.

It should be observed that, in contrast to the results reported on CoNi-molybdate catalysts [6], the additives of the transition metal ions to the supported molybdena catalysts lead to the increase of not only the activity but also the selectivity to propene. Again, further studies (now in course), aiming at determination of physico-chemical properties of the catalysts are necessary to discuss the reason of the ameliorating effect of the additives.

The data for the mixed V–Mo–O/SiO_2 catalysts are presented in Table 5. Considerable increase in the activity for both mixed V–Mo–O preparations as compared with MoSi and KMoSi catalysts can be observed, the propane conversion at both reaction temperatures being considerably higher for the former catalysts in spite of the lower contact time. This is in keeping with the fact that vanadia-based catalysts are usually more active in the ODH of propane (show the measurable activity already at temperatures ~350°C) than the molybdena-based catalysts, the latter beginning to show the activity at temperatures > ~500°C [10,11]. Out of the two samples, this of higher Mo/V ratio was more selective (at comparable conversions), its selectivity being close to that of the MoSi catalyst. Thus, the addition of some vanadium oxide phase may lead to a better performance (higher yields of propene) of MoO_x/SiO_2 catalysts.

Table 5. Oxidative dehydrogenation of propane on K Mo–V–O/SiO_2 catalysts.

Catalyst	Temperature [°C]	τ [s]	Conversion [%]	Selectivity [%]		
				C_3H_6	CO_2	CO
K1Mo0.5VSi	500	0.50	12.8	45.1	25.1	29.9
		0.33	7.2	58.4	25.5	15.9
		0.25	5.9	68.5	19.4	12.2
	520	0.50	20.2	40.2	23.8	36.1
		0.33	15.1	51.7	20.2	28.2
		0.25	11.4	59.6	18.0	22.5
K0.75Mo1.5VSi	500	0.50	11.4	35.9	21.1	43.1
		0.33	7.0	53.2	12.0	34.9
		0.25	5.0	63.4	11.5	25.1
	520	0.50	18.2	31.7	18.8	49.5
		0.33	13.3	44.1	14.5	41.4
		0.25	10.5	50.8	13.4	35.8

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REFERENCES

1. Kung H.H., *Adv. Catal.*, **40**, 1 (1994).
2. Albonetti S., Cavani F. and Trifirò F., *Catal. Rev. Sci. Eng.*, **38**, 413 (1996).
3. Cavani F. and Trifirò F., *Catal. Today*, **36**, 431 (1997).
4. Mamedov E.A. and Cortés Corberán V., *Appl. Catal.*, **127**, 1 (1995).
5. Mazzochia C., Aboumrad C., Diagne C., Tempesti E., Herrnan J.M. and Thomas G., *Catal. Letters*, **10**, 181 (1991).
6. Stern D.L. and Grasselli R.K., *J. Catal.*, **167**, 550; 560 (1997).
7. Lezla O., Bordes E., Courtine P. and Hecquet G., *J. Catal.*, **170**, 346 (1997).
8. Lee K.H., Yoon Y.S., Ueda W. and Moro-oka Y., *Catal. Letters*, **46**, 267 (1997).
9. Yoon Y.S., Suzuki K., Hayakawa T., Hamakawa S., Shishido T. and Takehira K., *Catal. Letters*, **59**, 165 (1999).
10. Grzybowska B., Mekšs P., Grabowski R., Wcisło K., Barbaux Y. and Gengembre L., *Stud. Surf. Sci. Catal.*, **82**, 151 (1994).
11. Grabowski R., Grzybowska B, Samson K., Słoczyński J., Stoch J. and Wcisło K., *Appl. Catal. A: General*, **125**, 129 (1995).
12. Meunier F.C., Yasmeen A. and Ross J.R.H., *Catal. Today*, **37**, 33 (1997).
13. Chen K., Xie S., Bell A. and Iglesia E., *J. Catal.*, **195**, 244 (2000).
14. Grzybowska-Świerkosz B., *Topics Catal.*, **21**, 35 (2002).
15. Blasco T. and López Nieto J.M., *Appl. Catal. A: General*, **157**, 117 (1997).
16. Klisińska A., Haras A., Samson K., Witko M. and Grzybowska B., *J. Mol. Catal.*, (in press).
17. Abello M.C., Gomez M.F. and Cadus L.E., *Catal. Letters*, **53**, 185 (1998).
18. Samson K., Klisińska A., Gressel I. and Grzybowska B., *React. Kinet. Catal. Lett.*, **77(2)**, 309 (2002).
19. Słoczyński J., Grabowski R., Wcisło K. and Grzybowska-Świerkosz B., *Polish J. Chem.*, **71**, 1585 (1997).
20. Kim D.S., Wachs I.E. and Segawa K., *J. Catal.*, **146**, 268 (1994).
21. Deo G., Wachs I.E. and Haber J., *Critic. Rev. Surf. Chem.*, **4**, 141 (1994).
22. Wachs I.E., *Catal. Today*, **27**, 437 (1996).
23. Grzybowska-Świerkosz B., *Appl. Catal. A*, **157**, 263 (1997).