Catalytic activity of unpromoted and promoted nickel molybdate in butane selective oxidation

Manuel F. Portela,[a] R. Martin Aranda,[a] Miguel Madeira,[a] M. Oliveira,[a] Felipe Freire,[a] Riccardo Anouchinsky,[b] Abdelhakim Kaddouri[b] and Carlo Mazzocchia*[b]

[a] *GRECAT, Instituto Superior Tecnico, Lisbona, Portugal*
[b] *Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, Italy*

Stoichiometric α- and β-phases of NiMoO$_4$ show remarkable differences in the selective oxidation of butane to butenes and butadiene; modification of the surface acid–base properties of the catalysts by doping with K and Ca results in an increase in catalytic activity, especially with the α-phase

Stoichiometric nickel molybdate, NiMoO$_4$, has been proven to be a highly effective catalyst for the oxidative dehydrogenation of alkanes, especially propane.[1] For this reaction the octahedral α-phase, stable from room temperature to 923 K, is more active but less selective than the β-phase. The β-phase is formed at high temperature and is stable on cooling up to 473 K.[2] The intrinsic activity is greater for the high temperature β-phase, and better propene yields are obtained with that phase despite its lower surface area.[3]

There are very few catalytic systems known to be active for lower alkane partial oxidation, and NiMoO$_4$ based systems could offer a valid alternative to the VPO catalysts successfully studied in the case of C$_4$–C$_5$ hydrocarbons,[4,5] provided good activity and selectivity are maintained. For this reason the procedure adopted for the catalyst preparation is of particular importance as different stoichiometric precursors can be obtained having different catalytic performances.[6]

In the case of propane partial oxidation, considerable improvements in selectivity have been obtained by promoting the catalyst with alkaline and alkaline-earth elements. This is mainly due to the increase in basicity of the catalytic surface which favours the desorption of the olefin and limits its conversion to further oxidation products.[7]

The same experimental approach was used for the study of butane partial oxidation; stoichiometric NiMoO$_4$ catalysts were prepared from yellow precursors[6] and K or Ca addition carried out by a conventional capillary impregnation procedure.

Catalytic runs were performed using a flow system with a fixed bed quartz reactor (I.D. 20 mm; length 600 mm). All experiments were conducted at atmospheric pressure at 648–848 K. The tests with the β-NiMoO$_4$ were carried out first by heating the α-NiMoO$_4$ at 983 °K in an air flow for 10 min in order to complete the phase transition, and then cooling to the desired temperature. The feed was composed of a mixture of butane, oxygen and nitrogen with a molar ratio of 4:9:87. Analysis of the reactants and products was carried out by gas chromatography.

Table 1 shows the effect on the surface acid–base properties of the α-nickel molybdate due to impregnation with Ca and K, measured by the isopropanol catalytic decomposition reaction under steady state conditions in the absence of air (T = 180 °C). It was observed that the ratio between propene and acetone produced became smaller after the addition of promoters, indicating that there was a significant increase of the number of

Table 1 Isopropanol decomposition on undoped and doped α- NiMoO$_4$

Sample	Surface area/ m^2 g^{-1}	Propene/ μmol h^{-1} m^{-2}	Acetone/ μmol h^{-1} m^{-2}
α-NiMoO$_4$	32.2	11.0	3.1
α-NiMoO$_4$/2% Ca	28.9	9.0	6.1
α-NiMoO$_4$/0.2% K	30.7	6.6	4.9

Table 2 Selectivities at 12% conversion of undoped and doped α-NiMoO$_4$

	Selectivity						
Sample	CO	CO$_2$	but-1-ene	*trans*- but-2-ene	*cis*- but-2-ene	butadiene	ΣC$_4$
α-NiMoO$_4$	26.6	31.6	7.1	7.5	6.5	20.7	41.8
α-NiMoO$_4$/0.2% K	17.0	26.5	10.9	9.2	10.1	26.3	56.5
α-NiMoO$_4$/2% Ca	17.8	27.9	8.6	8.5	8.2	29.0	54.3

Contact time = 2 g$_{\mathrm{cat}}$ h/mol butane.

Table 3 Selectivities at 12% conversion of undoped and doped β-NiMoO$_4$

	Selectivity						
Sample	CO	CO$_2$	but-1-ene	*trans*- but-2-ene	*cis*- but-2-ene	butadiene	ΣC$_4$
β-NiMoO$_4$	9.0	10.0	18.8	16.0	16.7	29.5	81.0
β-NiMoO$_4$/0.2% K	11.3	8.6	20.8	14.5	17.8	27.2	82.3
β-NiMoO$_4$/2% Ca	6.2	9.0	20.6	14.8	16.2	33.1	84.7

basic sites on the surface of the catalyst. These measurements could not be done with the β-phase as it is not stable at the temperature used for the isopropanol tests. Table 2 shows the catalytic results measured at 12% conversion for the α-phase before and after doping and shows a considerable activity improvement due to promoter addition. The indicated weight percentages of the doping elements reported were those that gave the best catalytic results.

In the case of propane, the β-phase proved to be the most selective for all the tested samples (Table 3), leading to higher selectivities of C_4 products, particularly butadiene. This fact is quite relevant when considering the diminution of the surface area of the high temperature β-phase, whose intrinsic activity for butane partial oxidation becomes much greater with respect to the α-phase than in the case of propane.[3] The addition of promoters in this case resulted in a small increase in C_4 selectivities at isoconversion. This can be explained by the very high catalytic performance of the unpromoted β-phase. The main noticeable effect was a marked decrease in carbon monoxide production observed with the Ca doped β-$MiMoO_4$ catalyst.

References

1 C. Mazzocchia, Ch. Aboumrad and E. Tempesti, *Fr. Pat.*, 8 900 522, 1989.
2 C. Mazzocchia and F. Di Renzo, *Thermochim. Acta*, 1985, **85**, 139.
3 C. Mazzocchia, Ch. Aboumrad, C. Diagne, E. Tempesti, J. Herrmann and G. Thomas, *Catal. Lett.*, 1991, **10**, 181.
4 P. Michalakos, M. Kung, I. Jahan and H. Kung, *J. Catal.*, 1993, **140**, 226.
5 G. Hutchings, R. Olier, M. Sananes and J. C. Volta, *New Development in Selective Oxidations*, ed. V. C. Corberan, Benalmadema, Elsevier, 1993.
6 C. Mazzocchia, R. Anouchinsky, A. Kaddouri, M. Sautel and G. Thomas, *J. Therm. Anal.*, 1993, **40**, 1253.
7 C. Mazzocchia, A. Kaddouri and R. Anouchinsky, unpublished data.

Received, 6th October 1995; Com. 5/06593C