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V–Mg–O catalysts for oxidative dehydrogenation of alkylpyridines and alkylthiophenes

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ABSTRACT

Vanadium appears to be the element that is most frequent (along with molybdenum) used in the catalyst formulations for oxidative dehydrogenation (ODH) of hydrocarbons and alcohols. In the present work the employment of ODH reaction in the presence of air has been extended for the preparation of vinyl substituted pyridines and thiophenes using vanadium (and for comparison molybdenum) oxide catalysts.

The efficiency of vanadium–magnesium oxide catalysts in the production of vinylpyridines and vinylthiophenes has been evaluated. A strong dependence of the yield and selectivity of the latter upon the vanadium (molybdenum) oxide loading and the conditions of heat treatment were observed. In optimized reaction conditions V–Mg–O catalysts at the temperature approximate 450 °C ensured the formation of vinylpyridines and vinylthiophenes with the yield of 40–60% at the selectivity of 90%. In prolonged runs no visible changes in the performance of the catalyst were observed. DTA–DTG, XRD, IR ESR, NMR methods have been used detecting the formation of species of V–Mg–O catalysts that appear to be responsible for the catalyst efficiency in the reactions under consideration.

1. Introduction

Oxidative dehydrogenation (ODH) continues to be an interesting alternative to the usual dehydrogenation. V–Mg–O catalysts are known to be active and selective in ODH of alkylbenzenes and lower alkanes [1,2].

Compared with conventional dehydrogenation, higher degrees of conversion and selectivity have been achieved for ODH of alkylaromatic compounds and alcohols. However, for the ODH of alkanes, in particular of propane, the problem of developing efficient catalysts remains unsolved due to the low selectivity to alkenes [2–4].

There are data that for ODH of hydrocarbons the optimal catalysts differ not only in the vanadium (molybdenum) oxide loading but in the preparation mode as well. It was of interest to investigate this problem extending ODH reaction to compounds of some other classes, namely to alkyl substituted heterocycles.

Vinyl pyridines and vinylthiophenes are important intermediates for the production of some polymeric, composite materials [5] and for fine chemistry. The main method for their production is dehydrogenation of alkyl-substituted heterocycles. Information on the synthesis of vinylphyridines or thiophenes using ODH is scanty [6,7], and yields of the target products are not sufficient.

In the present work the reaction of ODH has been used to obtain vinyl substituted heterocyclic compounds (pyridines and thiophenes) using vanadium oxide catalysts in the presence of air as the oxidant. Effect of the structure of the catalyst and method of it pretreatment on the efficiency in ODH has been investigated.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by impregnation of commercial MgO (BET surface area about 100 m^2/g) with corresponding ammonium salts. MgO was powdered and suspended in an aqueous solution of ammonium vanadate at 40–60 °C under stirring. The obtained material was evaporated (60 °C), dried in air (120 °C), subjected to the further treatment in airflow by the stepwise temperature increase. At 150, 260, 360, 400, and 500 °C the samples were kept for 1 h, and for 3–4 h at the terminal temperature. The latter varied from 550 to 850 °C. The powder formed was pressed into the tablets and crushed into pieces of a required size.

2.2. Catalyst characterization

BET surface areas were determined by N_2 physisorption at the temperature of liquid nitrogen.

X-ray diffraction was studied using a Guinier–Hagg focusing camera Fr-552 and automatic powder X-ray diffractometer

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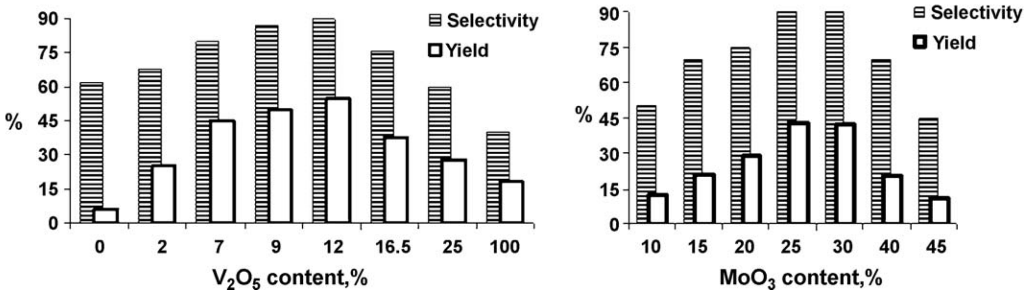

Fig. 1. The effects of V_2O_5 and MoO_3 loading on ODH of 2-ethylpyridine (420 °C, LHSV of 1.5 h^{-1}, 2-ethylpyridine/O_2 = 1/1).

"STADI-P" with imaging plate (Cu Kα radiation, 2θ range was from 7° to 60°).

DTA–DTG analysis was performed in the air flow at the temperature range of 20–1000 °C using MDTA 85 SETARAM apparatus. The heating rate was of 5 °C/min.

IR spectra were recorded by a "Specord 75IR" instrument using the mineral oil disc technique and calibrated amounts of the samples (5% by wt.) in the region 4000–200 cm^{-1}. The spectra were recorded in air using a 2 cm^{-1} resolution.

2.3. Catalyst testing

The catalysts were tested in a fixed bed quartz reactor, varying the reaction conditions (viz., temperature, LHSV, heterocycle/O_2 mole ratio). The catalyst samples with particle diameter of 0.5–1.0 mm were mixed with quartz particles in the volume ratio of 1:2.

The reaction products were determined by chromatographic analysis. A column filled with Porapak Q (80–100 mesh) was used for the analysis of alkyl- and vinyl-substituted heterocycles, CO_2, and O_2. The other column filled with molecular sieves 5 A, was used for the analysis of CO, CH_4, O_2, and CO_2. The amount of compaction products was determined by the derivatographic assay method.

3. Results and discussion

In the present work the reaction of ODH is extended on alkyl-substituted heterocyclic compounds (alkyl pyridines and alkyl thiophenes) using vanadium (and for comparison molybdenum) oxide catalysts. Effect of the composition of the catalyst and of the method of its preparation (pretreatment) on the efficiency of the reaction has been investigated.

The primary testing of V–Mg–O catalysts has revealed that ODH of alkyl-substituted heterocycles proceeded selectively in a temperature range 250–500 °C, the major reaction product being vinyl-substituted heterocycles. Pyridine, pycolines, methylthiophene and thiophene were detected in minor amounts (up to 1%).

We have found previously for the ODH of hydrocarbons and alcohols that the activity and selectivity of V–Mg–O catalysts depended significantly on the vanadium loading as well the conditions of thermal treatment of the sample [1,8].

A series of catalysts has been prepared to investigate the influence of both factors on the ODH of substituted heterocycles, and to identify the optimal catalysts composition and the thermal treatment mode. The vanadium and molybdenum loading were varied from 5 to 85% and from 5 to 45%, respectively, the thermal treatment was changed from 550 to 850 °C. The results are presented in Figs. 1 and 2.

With increasing the V_2O_5 content (5–85%) in the samples treated at 550 °C the conversion of 2-ethylpyridine passed a maximum at 12%. As a result, in case of vanadium pentoxide loading of 12% the dependences of the vinylpyridine yield and selectivity characterized by clear peaks (55 and 90%, respectively). For molyblenum oxide catalysts the peak corresponded to 25–30% of MoO_3 loading.

The extremal dependence of the catalyst performance from the catalyst pretreatment was found for both V_2O_5 and MoO_3 catalytic systems. The maximum of conversion and selectivity, in ODH was observed on the catalysts treated at 550 °C. Further increasing the thermal treatment temperature to 750–850 °C resulted in a drastic decrease of the conversion and the selectivity to vinylpyridine. Thus, the catalytic properties of both systems in ODH of alkyl pyridines are similar, but the MoO_3 catalysts appeared to be a little less active in comparison to the V_2O_5 ones. Over V–Mg–O catalysts in optimum reaction conditions the selectivity to vinyl pyridines and vinyl thiophenes varied, depending on their structure, and achieved of 80–90% at the conversions of 50–60%. The catalysts operated in oxidative dehydrogenation steadily without reducing the activity and selectivity towards 2-ethylpyridine in a prolonged run. After 30–40 h on stream the catalyst kept the initial activity (Fig. 3).

A slight dependence of the performance of the V–Mg–O catalysts from the structure has been observed. As concerns the relative reactivity, the examined alkyl pyridines and alkyl thiophenes can be arranged into the rows, namely: 2-ethylpyridine > 4-ethylpyridine > 2,5-diethylpyridine > 2-isopropylpyridine > 2-methyl-

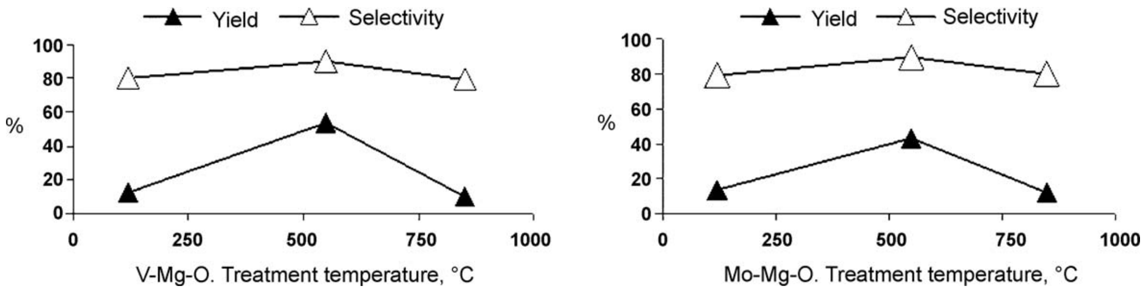

Fig. 2. The effects of heat treatment on the efficiency for ODH 2-ethylpyridine.

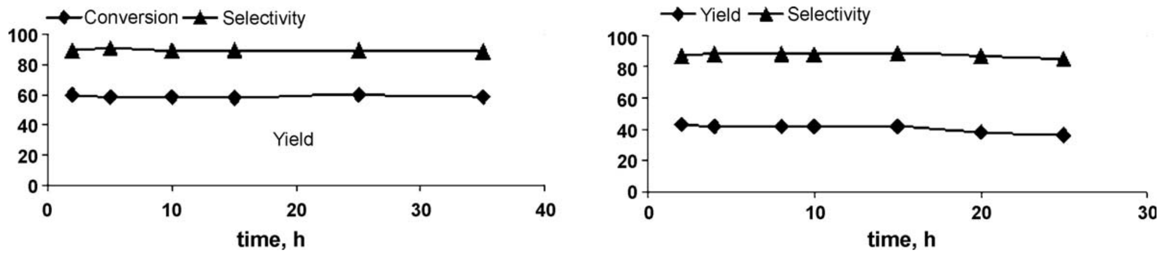

Fig. 3. OD 2-ethylpyridine in a prolonged run over V-MgO, MoO3 catalysts (420 °C, LHSV of 1.5 h^{-1}, 2-ethylpyridine/O_2 mole/O_2 1/1).

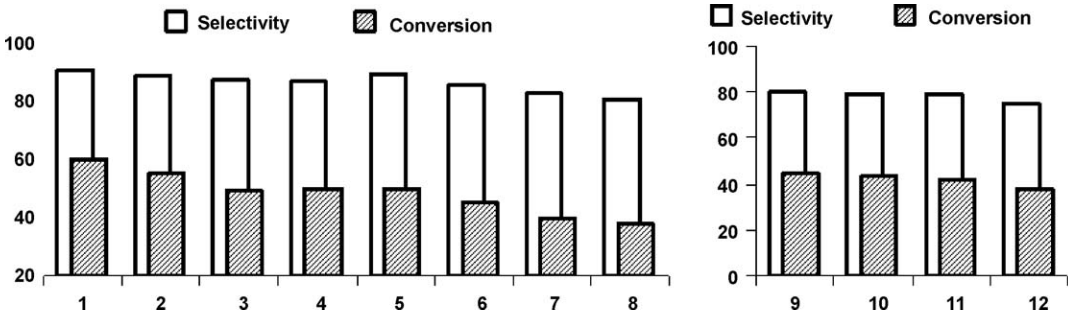

Fig. 4. (1–8) Comparative reactivities of alkyl pyridines: (1) 2-ethylpyridine > (2) 4-ethylpyridine > (3) 2,5-diethylpyridine > (4) 2-isopropylpyridine > (5) 2-methy-5-ethylpyridine > (6) 2-methyl-5-butylpyridine > (7) 2-propylpyridine > (8) 2-butylpyridine. (9–12) Comparative reactivities of alkyl thiophenes: (9) 2-ethylthiophene > (10) 2-isopropylthiophene > (11) 2-propylthiophene > (12) 2-butylthiophene.

5-ethylpyridine > 2-methyl-5-butylpyridine > 2-propylpyridine > 2-butylpyridine; 2-ethylthiophene > 2-isopropylthiophene > 2-propylthiophene > 2-butylthiophene (Fig. 4).

Thus, the reaction of ODH in the presence of air has been used to obtain vinyl substituted heterocyclic compounds (pyridines and thiophenes) using vanadium (and for comparison molybdenum) oxide catalysts. Effects of the composition of the V–Mg–O catalysts and the method of their heat pretreatment on the efficiency of the reaction have been investigated. V_2O_5 content of 12 wt.% and a rather low calcination temperatures (550 °C) are found to be advantageous for ODH of pyridines and thiophenes. Quite similar situation have been observed earlier for ODH of other compounds with activated C–H bonds, such as alkylbenzenes and alcohols [1,8]. Obviously the features of the surface structure of the catalysts required for all these reactions should be identical and a joint consideration of them seems to be expedient.

Next the catalyst samples used in ODH of pyridines and thiophenes were subjected to characterization by DTG–DTA, XRD methods, IR spectra.

DTG–DTA analysis was useful to get an idea on the processes that proceeded in the catalyst during its thermal treatment up to 800 °C. Endoeffects at 225, 255, and 360 °C were observed when a catalyst was gradually heated up to 400 °C. These effects followed by a weight loss reflect the elimination of water and ammonia. Apparently, MgO impregnated by NH_4VO_3 generate no additional substances in the temperature range mentioned. During the further increasing the temperature exoeffects at 408, 655, and 775 °C that were not followed by a weight loss. They are believed to reflect interactions between the active component and the support (apparently the formation of magnesium vanadates). Interestingly, the effect at 408 °C is more pronounced for the samples with a V_2O_5 loading of 12%, whereas the effects at 655 and 775 °C are pronounced for the samples with vanadium loading of 25%. The interaction was apparently completed before the temperature reached 800 °C. To interpret the nature of the vanadates the samples were subjected to XRD investigations.

X-ray diffraction pattern for catalysts containing 12% V_2O_5 and calcined at 550 °C is shown in Fig. 5. Besides the dominating diffraction lines of MgO (2(= 45, 65) the spectrum revealed the diffraction lines of 2(= 18.9, 28.2, attributed to (-$Mg_2V_2O_7$ (ASTM file 31-816), and weak lines of 2(= 20.69, 26.2, 26.31, 31.06, 53, and 66 attributed to (-$Mg_3V_2O_8$ (ASTM file 37-351). For the catalyst with the V_2O_5 content of 25% calcined at 850 °C (Fig. 6), lines attributed to (-$Mg_2V_2O_7$ (2(= 18.9, 28.2) became very weak, whereas lines of 2(= 20.69, 26.2, 26.31, 31.06, 53, and 66 (attributed to (-$Mg_3V_2O_8$) became more pronounced. These results are in agreement with results obtained [9] where was shown that

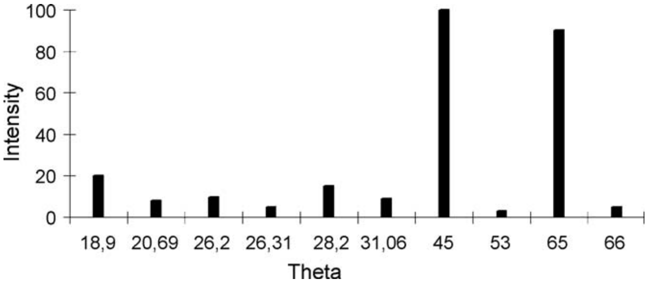

Fig. 5. X-ray diagram of V–Mg–O catalyst (V_2O_5 content of 12%, thermal treatment at 550 °C).

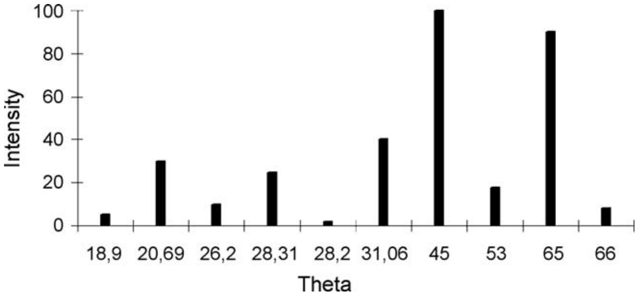

Fig. 6. X-ray diagram of V–Mg–O catalyst (V_2O_5 content of 25%, thermal treatment at 850 °C).

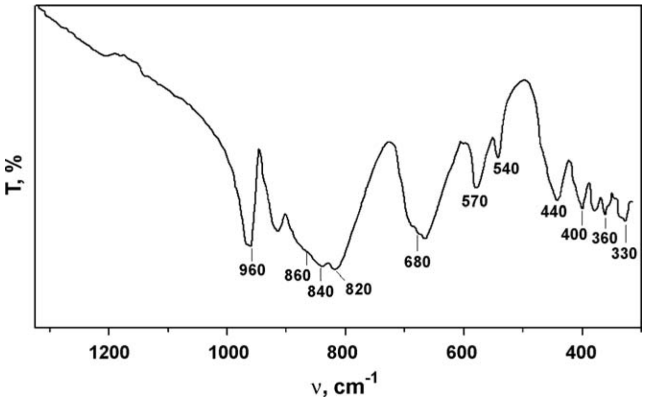

Fig. 7. IR spectra of the V–MgO catalyst calcined at 550 °C.

the formation of $Mg_2V_2O_7$ occurs at about 410 °C, whereas the formation of $Mg_3V_2O_8$ necessitate heating to 600–800 °C.

The above XRD data correspond with the data IR spectrum of the V–MgO catalyst with a V_2O_5 content of 12% after calcination at 550 °C shows the bands at 820, 860, and 960 cm^{-1} (intense), and there bands at 330, 360, 400, 440, 540, 570, and a broad band in the range of 440 cm^{-1} appeared (Fig. 7). The band at 960 cm^{-1} (intense) is attributed to the V═O bond in the disturbed octahedron characteristic for $Mg_2V_2O_7$ [10]. The band at 860 cm^{-1} is attributed to the V–O–V bond in the ortho-vanadate ($Mg_3V_2O_8$) with VO_4^{3-} ions in the tetrahedral environment. The bands at 680 and 540 cm^{-1} can be attributed either to V–O–V bond, or to the V^{+5} ions in the octahedral environment [10]. The broad band at 440 cm^{-1} can be attributed to MgO.

The catalyst with V_2O_5 content of 25% shows bands in the range of 860 cm^{-1} and 1020–1050 cm^{-1}. The broad band at 860 cm^{-1} is attributed to the V–O–V bond in the ortho-vanadate ($Mg_3V_2O_8$) with the VO_4^{3-} ions.

IR spectroscopic data are in good agreement with those obtained by X-ray diffraction.

The existence of a number of vanadium coordination states on the catalyst surface was established using ^{51}V NMR [12]. Their relative concentrations are determined by the loading (surface concentration) of vanadium. The isolated tetrahedral and octahedral vanadium species appear even at low vanadium content (5% V_2O_5). These species are supposed to provide complete oxidation. At the V_2O_5 loading of 12%, the associated vanadium forms predominate. In these associated species, vanadium may exist in both octahedral and tetrahedral environment. We suggest the associated species favour the ODH of alkyl heterocyclic compounds. At higher vanadium loading (25% V_2O_5) the phase of magnesium ortho-vanadate $Mg_3V_2O_8$ predominates that apparently does not favour the selective ODH.

In the ESR spectra recorded at 77 K of the catalysts treated in O_2 at 773 K, a signal with parameters $g_{||} = 1.95$, $A_{||} = 170$ G is observed. It was attributed to V(IV) in distorted tetrahedral oxygen environment [12]. This observation was supplemented with the results of ^{51}V NMR investigation. A conclusion was drawn, that on the catalyst surface there exist various vanadium species, which differ in the structure of their local environment. Evidently along with pyrovanadates and ortho-vanadates V forms tetrahedral and octahedral surface complexes, which form associated surface species. At low vanadium content, V(V) produces isolated tetrahedral and octahedral surface complexes, these do form associated surface species as the vanadium content increase. In these associated complexes, vanadium may exist in tetrahedral and octahedral environments. The amount of tetravalent vanadium observed does not exceed 2–5% of the total vanadium content and is hardly supposed to be essential for the target reaction [12].

The results of DTA–DTG, XRD, and IR, ESR spectroscopy, and of ^{51}V NMR demonstrate that catalyst with a V_2O_5 content of 12% and treated at 550 °C favour the predominant formation of magnesium vanadates with irregular structure, apparently of the pyrovanadate type ($Mg_2V_2O_7$) with vanadium ions V^{5+} and V^{4+} in the octahedral coordination. They exhibit high activity in the process of the oxidative dehydrogenation of alkyl heterocyclic compounds. Similar conclusion was drawn for the ODH of alcohols over V–Mg–O catalyst [9,10].

Thus, it turns out that the ODH of compounds with activated C–H bonds (alkylsubstituted heterocycles, of alcohols [10,11] and of ethylbenzene [1,2]) requires identical active phase species responsible for the high efficiency of the catalyst. These species are suggested to be magnesium vanadates apparently of the pyrovanadate type with an irregular structure, and V-ions in the octahedral coordination. They are predominantly formed when the catalysts with 12% V_2O_5 are pretreated at 550 °C.

4. Conclusions

The reaction of ODH in the presence of air has been extended on alkyl substituted heterocyclic compounds (pyridines and thiophenes) to produce corresponding vinyl derivatives. A method of preparation for highly active, selective and stable V–Mg–O catalysts has been elaborated. The selectivity to vinyl pyridines and vinyl thiophenes at optimal reaction conditions achieved of 90% at the conversion of 50–60%.

The efficiency of catalysts V–Mg–O and Mo–Mg–O substantively depends on the active component (V_2O_5, MoO_3) loading and the conditions of heat pretreatment. The optimal loading of V_2O_5 and MoO_3 were of 12 and 25%, respectively, and heat pretreatment temperature was of 550 °C.

V–Mg–O catalysts revealed good stability. In prolonged runs during 40 h of operation no visible decline of activity was detected, the average yield and selectivity were of 50–56% and 90%, respectively.

The role of magnesium vanadates with irregular structure, apparently of the pyrovanadate type ($Mg_2V_2O_7$) with vanadium ions V^{5+} and V^{4+} in octahedral coordination in ODH of compounds with activated C–H bonds is discussed.

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