Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS

J. Serb. Chem. Soc. *73* (1) 55–64 (2008)
JSCS–3687

UDC 546.881–31+546.77–31+547.214:544.4
Original scientific paper

Selective oxidation of isobutane on V–Mo–O mixed oxide catalysts

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(Received 30 November 2006, revised 4 September 2007)

Abstract: Four V–Mo–O mixed metal oxides were prepared, characterized and tested for the selective oxidation of isobutane in the temperature range 350–550 °C, at atmospheric pressure. Isobutane was mainly oxidized to *iso*-butene and carbon oxides. The systems with low vanadium contents showed low activities but high isobutene selectivities, while the systems with high vanadium contents showed high activities with high carbon oxides selectivities. The effects of temperature, contact time and the molar ratio *iso*-butane to oxygen on the conversion of isobutane and the selectivity of the oxidation were studied.

Keywords: vanadium molybdenum oxides; *iso*-butane oxidation; *iso*-butene.

INTRODUCTION

Selective oxidation of light alkanes is one of the most challenging topics for study because of the difficulty in stopping the oxidation at intermediate stages corresponding to olefin or oxygenates formation.

The development of more active and selective catalysts for the partial oxidation of alkanes has been extensively pursued in both industrial and academic research.[1,2]

In the literature,[3–8] several catalysts with different contents of V_2O_5 and MoO_3 have been studied for the selective oxidation of isobutane in order to determine the catalytically active phases. Thus, different oxide species were reported to be part of the active phase system in these catalysts. Andrushkevich[3] revealed MoO_3 and V_2O_4 as the major components of V–Mo–O catalysts and reported that the catalytic activity is related to the content of V^{4+}. Tichy *et al.*[4] identified VMo_3O_{11}, whereas Werner *et al.*[5] proposed VMo_4O_{14} as the active phase. Both mixed oxides build layered structures, belonging to shear structures.

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doi: 10.2298/JSC0801055M

Werner *et al.*[5] explained that these structures are able to integrate and remove oxygen by a transition from corner-linked octahedra into edge sharing regions.

A key aspect towards the application of this type of catalysts is the exploration of how to control the operating conditions in order to maximize the catalytic performance (temperature, isobutane-to-oxygen molar ratio, hourly space volume velocity). It is commonly accepted that highly specific, local electronic structures of the active metal sites are essential for the catalytic performance.[9] The catalyst composition, as well as the conventional optimization of the microstructure by optimizing the synthesis procedure could result in further improvement of the catalytic performance. Hoang *et al.*[10] showed that alumina-supported vanadia exhibits low (15 %) selectivity to isobutene. An olefin selectivity of about 50 % was achieved at isobutane conversions of 10–15 % over vanadium-containing MCM-41 mesoporous catalysts.[11,12]

Good results for the oxidative dehydrogenation of isobutane were also obtained with heteropoly compounds[13–17] and pyrophosphates.[18,19]

The aim of this work was to study ways of enhancing the catalytic performance of V–Mo–O mixed oxide catalysts in the isobutane oxidation process, by adjusting the operating conditions and the catalyst composition. Thus, the influence of temperature, space velocity and feed composition on the catalytic performance of four V–Mo–O systems were investigated.

EXPERIMENTAL

Preparation and characterization of the catalysts

Mo–V–O-based catalysts, with the calculated compositions listed in Table I, were prepared from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.8 %) and NH_4VO_3 precursors using the same method as reported by Ueda *et al.*[20]

The $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.8 %) and NH_4VO_3 precursors were dissolved seperately in distilled water and the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution was added to the NH_4VO_3 solution. For all the samples, the obtained mixture was heated at 90 °C to evaporate the water and then the remaining solid was dried at 120 °C for 15 h and calcined at 200 °C for 2 h, 400 °C for 2 h and 600 °C for 4 h, to obtain the final catalyst. For all the preparations, the same method and the same calcination temperatures were employed knowing that the preparation method and the calcination temperature influence the phase composition of Mo–V-oxides.[21-23]

The symbols used to denote the prepared catalysts are listed in Table I.

TABLE I. The calculated catalyst compositions and the symbols used

Catalyst	Calculated catalyst composition
C_1	10 % V_2O_5–90 % MoO_3
C_2	30 % V_2O_5–70 % MoO_3
C_3	50 % V_2O_5–50 % MoO_3
C_4	90 % V_2O_5–10 % MoO_3

The surface areas of the catalysts were measured from the adsorption isotherms of N_2 at 77 K using the BET method with an ASAP 2000 sorptometer. The crystal structures of the samples were controlled by X-ray diffraction using a PW 3710 diffractometer with CuK_{α} radiation for Bragg's angles (2θ) from 4 to 70°.

Catalytic reactions

The selective oxidation of isobutane was carried out in a fixed bed, quartz tube, down-flow reactor operating at atmospheric pressure. The internal diameter of the reactor tube was 20 mm. The catalyst was supported by quartz wool. Normally, 2 cm^3 (1.7 g) catalyst was used. The axial temperature profile was measured using a chromel–alumel thermocouple placed in a thermowell centered in the catalyst bed. The reactor temperature was controlled using a chromel–alumel thermocouple attached to the exterior of reactor. Quartz chips were used to fill the dead volumes below and above the catalyst bed to minimize potential gas-phase pyrolysis reactions at higher reaction temperatures. The reaction mixture, consisting of isobutane and air, was passed through the catalyst bed at a volume hourly space velocity (*VHSV*) of 1000–2500 h^{-1}. The influence of the isobutane to oxygen ratio was studied by varying this ratio in the range 0.5–2.0. The flow rates were controlled by fine needle valves and were measured using capillary flow meters. The catalyst was activated in air at 550 °C for 2 h before the reaction. Each run was carried out over a period of 3 h. In all studies, the reactor effluent passed through a condenser to remove water and liquid oxygenated products. The gas phase reactants and products were analysed as follows: a flame ionization detector and a GC- alumina column for the hydrocarbons and a thermal conductivity detector with a CTR-1 column for air, methane and carbon oxides. The condensate was analyzed with a Thermo Finnigan chromatograph using a DB-5 column and a flame ionization detector. Isobutene, CO, CO_2 were the major products formed under the employed reaction conditions; minor amounts of the liquid oxygenated products, acetic acid, methacrolein and unknowns were detected. The carbon balance was within 95–105 % for all of the reactions.

RESULTS AND DISCUSSION

Catalysts characterization

The XRD patterns of the prepared catalysts are shown in Fig. 1 and the observed phases are listed in Table II.

Examination of the powder diffraction patterns reveals the formation of multi-phase materials. Thus, in the 10 % V_2O_5–MoO_3 catalyst (C_1), three phases were observed, the MoO_3 phase being the predominant one. In the 30 % V_2O_5–MoO_3 catalyst (C_2), four phases were observed, the V_2MoO_8 phase being the predominant one. It should be noted that a V_2O_5 phase was not observed in these catalysts. In the catalyst with 50 % V_2O_5–MoO_3 (C_3), with four phases, the intensities corresponding to the V_2MoO_8 phase decreased and a V_2O_5 phase appeared. In the 90 % V_2O_5–MoO_3 (C_4) catalyst, with only two phases, the intensities of the V_2O_5 were the most dominant, while a MoO_3 phase was not observed.

The specific surface areas of the catalysts, obtained using the BET method, are presented in Table II. It can be observed that surface areas of all four catalysts were low, under 3 m^2 g^{-1}.

Catalytic properties

The four catalysts were tested in the selective oxidation of isobutane using an isobutane-to-oxygen ratio of 1. The conversion obtained and the distribution of the products are listed in Table III. From the results shown in Table III, it can be seen that the C_1 and C_2 catalysts revealed a similar activity for the conversion of isobutane. The same behavior was observed for the C_3 and C_4 catalysts. The catalysts containing the V_2O_5 phase, namely C_3 and C_4, were more active but less selective for isobutene. In these cases, higher quantities of CO_x were formed.

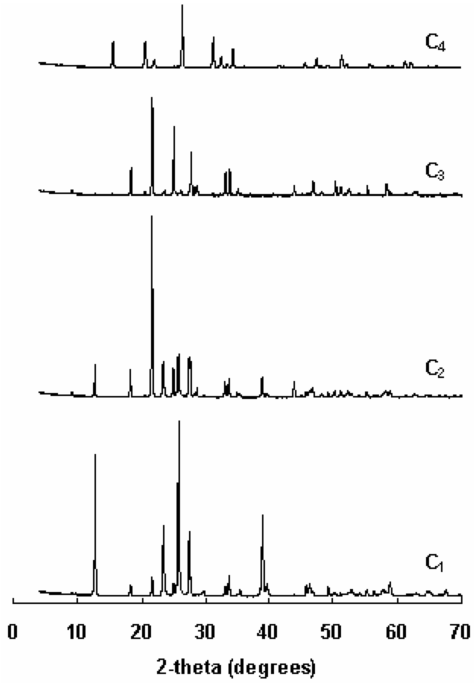

Fig. 1. X-Ray diffraction patterns of V–Mo mixed oxide catalysts.

TABLE II. The main crystalline phases determined by XRD and the specific surface areas of the V–Mo–O catalysts

Catalyst	*SSA* / m^2 g^{-1}	Crystalline phase identified				
C_1	1.81	MoO_3	V_2MoO_8	VO_2	–	–
C_2	1.63	MoO_3	V_2MoO_8	VO_2	–	$Mo_6V_9O_{40}$
C_3	0.94	MoO_3	V_2MoO_8	VO_2	V_2O_5	–
C_4	2.66	–	V_2MoO_8	–	V_2O_5	–

The selectivity of conversion to *iso*-butene for the C_1 and C_2 catalysts was appreciably higher than that for the C_3 and C_4 catalysts and the main over oxidation products were CO and CO_2. Oxygenated compounds were detected in a fairly low amount with the C_3 and C_4 catalysts and only traces at higher temperatures were found with the C_2 cataÿst. These two different ranges observed for *iso*-butene selectivity are probably related to the prevalence of two different catalytic sites on the surface. The most selective catalysts (C_1 and C_2) have isobutene selectivities that were about five times higher than the less selective one (the C_3 catalyst). Finally, it should be noted that cracking products were observed only with the C_1 catalyst and only at temperatures as high as 450 °C for space velocity of 2000 h^{-1}, or at temperatures higher than 490 °C with a space velocity of 2500 h^{-1}.

TABLE III. Catalytic performance of the V–Mo catalysts in the oxidation of isobutane (molar ratio i-C_4H_{10}:O_2 = 1:1)

Catalyst	$VHSV\times10^{-3}$ h^{-1}	t / °C	Conversion, %	Selectivity, %			Rate[a] mol kg^{-1} h^{-1}
			i-C_4H_{10}	i-C_4H_8	Oxigenated compounds	CO_x	
C_1	2.00	400	2.7	84.7	–	15.3	0.4
	2.00	450	5.2[b]	65.9	–	21.1	0.9
	2.50	400	1.7	85.3	–	14.7	0.3
	2.50	450	3.2	85.4	–	14.6	0.6
C_2	2.00	400	2.6	80.8	–	19.2	0.4
	2.00	450	3.2	62.9	11.6	25.5	0.5
	2.50	400	2.4	78.4	–	21.6	0.5
	2.50	450	2.9	57.0	2.4	40.6	0.6
C_3	2.00	400	9.2	18.3	6.2	75.5	1.5
	2.00	450	13.9	21.4	4.2	74.4	2.3
	2.50	400	8.1	14.1	2.3	83.6	1.6
	2.50	450	11.3	16.2	2.1	81.7	2.3
C_4	2.00	400	7.2	22.2	3.1	74.7	1.2
	2.00	450	9.6	25.4	2.1	72.5	1.6
	2.50	400	6.8	16.0	4.0	80.0	1.4
	2.50	450	8.5	38.2	2.6	59.2	1.7

[a]Reaction rate of isobutane; [b]selectivity to cracking products 13.1 %

The conversion of isobutane for the four catalysts as a function of reaction temperature is shown in Fig. 2. The conversion of *iso*-butane increased with increasing reaction temperature for all catalysts. The systems with a higher vanadium content (C_3 and C_4) were more active than the other two, over all the considered temperature range. Moreover, the V_2O_5 phase appeared only in these two catalytic systems and it is considered that this phase is responsible for the enhanced catalytic activity. No correlation was observed between the activity and the specific surface area of these catalysts.

The effect of the reaction temperature on the selectivities for *iso*-butene, CO_x and oxygenated products is shown in Fig. 3. Isobutene selectivity decreased with the temperature on the C_1 and C_2 catalysts, while, interesting, it increased for the C_3 and C_4 catalysts with increasing temperature. The latter phenomenon was also observed by Pless *et al.*[24] in the oxidative dehydrogenation of propane at temperatures higher than 400 °C and was related to the complete depletion of O_2 from the reactant stream, *i.e.*, when depletion of O_2 in the reactant stream occurs and as the temperature increases, a more efficient utilization of oxygen is realized, leading to an increase in selectivity. In the present case, the oxygen is far from completely depleted (Table III) which means that other factors must also be considered for explaining this phenomenon. The oxidative dehydrogenation of *iso*-butane to isobutene is more important over the C_1 and C_2 catalysts which contain mainly MoO_3 and V_2MoO_8 phases and do not contain a V_2O_5 phase. The selectivity for CO_x increased with increasing temperature on the C_1 and C_2 catalysts, while for the C_3 and C_4, the CO_x selectivity decreased with increasing temperature. The oxygenate compounds were detected in a fairly low amounts with the C_3 and C_4 catalysts and only traces were evidenced at higher temperature with the C_2 catalyst.

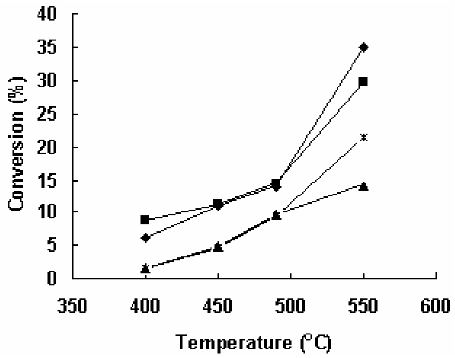

Fig. 2. Variation of the isobutane conversion with the reaction temperature over V–Mo–O catalysts ($VHSV$ = 1500 h^{-1}, molar ratio i-C_4H_{10}:O_2 = 1:1); ✳ – C_1; ▲ – C_2; ■ – C_3; ◆ – C_4.

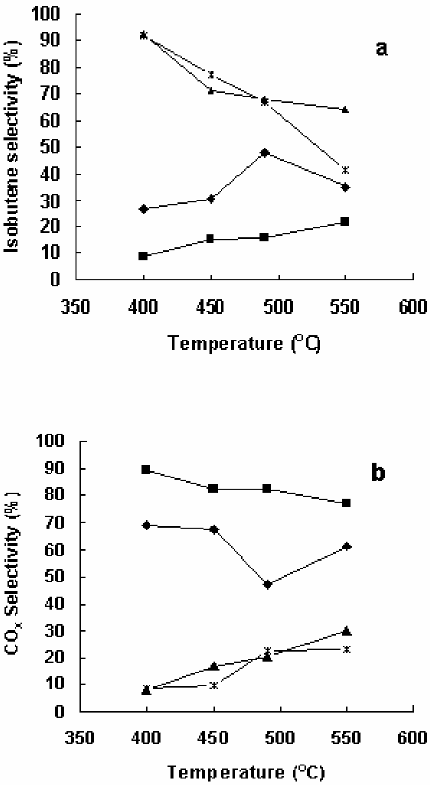

Fig. 3. Selectivity to: a) isobutene, b) CO_x and c) oxygenated products as function of temperature ($VHSV$ = 1500 h^{-1}, molar ratio i-C_4H_{10}:O_2 = 1:1); ✳ – C_1; ▲ – C_2; ■ –C_3; ◆ – C_4.

The variations of isobutane conversion and product selectivities as a function of the i-C_4H_{10}:O_2 molar ratio on the C_1 and C_3 catalysts at 400 °C are shown in Fig. 4. On the C_1 catalyst, the isobutane conversion was only slightly influenced by the i-C_4H_{10}:O_2 molar ratio and the isobutene selectivity passed through a maximum for the molar ratio 1:1. This maximum corresponds to a minimum of CO_x selectivity. For the C_3 catalyst, the isobutane conversion decreased clearly with the i-C_4H_{10}:O_2 molar ratio and the isobutene selectivity increased reaching a plateau at a ratio of around one. The CO_x selectivity decreased while the selectivity of oxygenates increased when the i-C_4H_{10}:O_2 molar ratio was increased. These results indicate that, with the C_3 catalyst, as the amount of oxygen was higher, the excess oxygen could oxidize a specific hydrocarbon species (adsorbed on the catalyst surface) to overoxidation products, such as CO and CO_2.

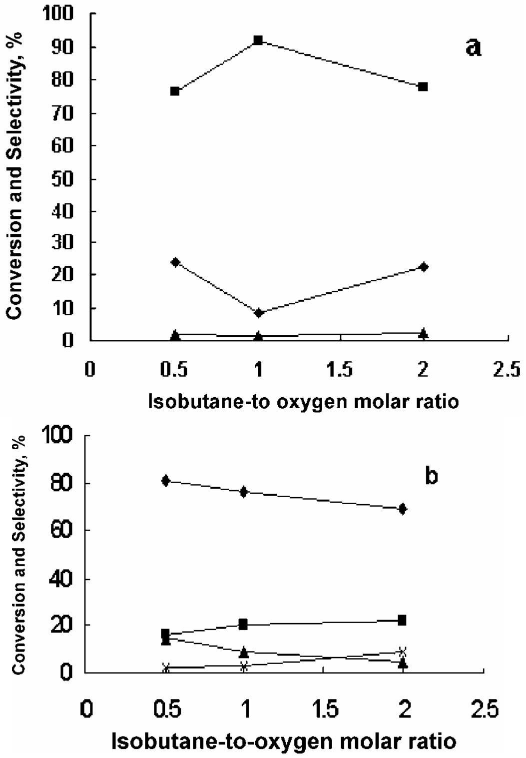

Fig. 4. Conversion of isobutane (▲) and selectivity to *iso*-butene (■), oxygenates (✳) and carbon oxides (◆) as function of i-C_4H_{10}:O_2 molar ratio over (a) C_1 catalyst and (b) C_3 catalyst at 400 °C, *VHSV* = 1500 h^{-1}.

The influence of the contact time on the conversion of isobutane and the isobutene and CO_x selectivities is shown in Fig. 5 for the C_1 catalyst at 450 °C. The conversion increased with increasing contact time, while the isobutene selectivity decreased. As expected, the operation at shorter contact time decreased the selectivity for overoxidation products and thus increased the selectivity to isobutene.

Finally, the apparent activation energies corresponding to the conversion of isobutane on the different catalysts under the same conditions (*VHSV* = 1500 h^{-1}; isobutane/oxygen = 1, t = 350–550 °C) were calculated and Arrhenius plots obtained, presented in Fig. 6. The activation energies on the C_1 and C_2 catalysts were 79 and 67 kJ mol^{-1}, respectively. The activation energies on the C_3 and C_4 catalysts were 38 and 50 kJ mol^{-1}, respectively. It can be observed that the activation energies on the catalysts containing a V_2O_5 phase were lower than those measured on the catalysts without a V_2O_5. The lowest apparent activation energy was observed on the C_3 system, which contained both V_2O_5 and MoO_3 phases. All these values are comparable with those presented in the literature for the same reaction over vanadia based catalysts[25] and other oxide-based catalysts.[26]

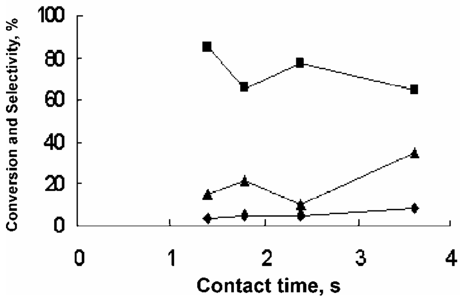

Fig. 5. Conversion of isobutane (◆) and selectivity to *iso*-butene (■) and CO_x (▲) as function of contact time over C_1 catalyst at 450 °C (molar ratio i-C_4H_{10}:O_2 = 1:1).

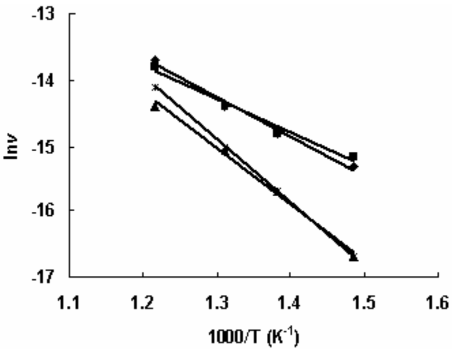

Fig. 6. Arrhenius plots for the conversion of isobutane on different catalysts: ✳ – C_1; ▲ – C_2; ■ – C_3; ◆ – C_4.

CONCLUSIONS

Four Mo–V–O based catalysts were examined for the selective oxidation of isobutane. A relationship between the phase composition of the catalysts and their oxidation of isobutane activity was evidenced. No correlation was observed between the activity and the specific surface area of these catalysts. The activity of the four studied catalysts increased with increasing content of vanadium. The C_3 and C_4 catalysts, containing a V_2O_5 phase, were more active but less selective, while the C_1 and C_2 catalysts were less active but more selective to *iso*-butene. On the C_3 and C_4 catalysts, total oxidation products (CO_x) were predominately obtained.

The oxygenates (acetic acid and methacrolein) were detected in a fairly low amount with the C_3 and C_4 catalysts and for the C_2 catalyst, only at high temperatures.

The conversion of isobutane increased with increasing reaction temperature for all catalysts and the isobutene selectivity decreased with the temperature on the C_1 and C_2 catalysts, while, interesting, for the C_3 and C_4 catalysts, it increased with increasing temperature. The *i*-C_4H_{10}-to-O_2 molar ratio was found to be optimum around a value of one. Operation at shorter contact time decreased the selectivity for the overoxidation products and thus increases the selectivity to isobutene.

The apparent activation energies for the transformation of isobutane were in the range 38–79 kJ mol^{-1}.

Acknowledgements. The authors are grateful to Dr. Éva Makó and Dr. Jozsef Kovacs for their expert technical assistance with the recording of the XRD spectra and the BET measurements, respectively. This research was supported by the National University Research Council (CNCSIS) under project No. 1064 A / 2006.

ИЗВОД

СЕЛЕКТИВНА ОКСИДАЦИЈА ИЗОБУТАНА НА V–Mo–O МЕШАНИМ ОКСИДНИМ КАТАЛИЗАТОРИМА

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У реакцији селективне оксидације изобутана припремљена су и тестирана у интервалу температуре 350–550 °C на атмосферском притиску четири металоксидна катализатора V–Mo–O. Изобутан се претежно оксидује до изобутена и CO_x. Системи са малим садржајем ванадијума показују малу активност али високу селективност у настајању изобутена, док системи са високим садржајем ванадијума показују високу активност и високу селективност у добијању CO_x. Испитиван је такође утицај температуре, времена контакта и моларног односа изобутана према кисеонику на конверзију изобутана и оксидативну селективност.

(Примљено 30. новембра 2006, ревидирано 4. септембра 2007)

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