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Influence of support and kind of VO_x species on isobutene selectivity and coke deposition in non-oxidative dehydrogenation of isobutane

Uwe Rodemerck *, Sergey Sokolov, Mariana Stoyanova, Ursula Bentrup, David Linke, Evgenii V. Kondratenko *

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29A, D-18059 Rostock, Germany

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ABSTRACT

Non-oxidative dehydrogenation of isobutane was investigated over VO_x/MCM-41, VO_x/Al_2O_3 and $VO_x/SiO_2–Al_2O_3$ (1–70 wt.% SiO_2). The highest selectivity to isobutene of around 85% at isobutane conversion of 50% was achieved over VO_x/Al_2O_3, while all other catalysts were significantly less selective and performed similarly to each other. The lower selectivity obtained on VO_x/MCM-41 and $VO_x/SiO_2–Al_2O_3$ is related to their higher activity for isomerization of isobutene to n-butenes as concluded from the results of separate tests with these olefins used as feed components. Our characterization studies suggest that the above isomerization reaction is catalyzed by both, Lewis acidic sites of support and VO_x species. Skeletal isomerization activity of the latter depends on their polymerization degree and indirectly affects coke formation because, in addition to isobutene, butadiene formed from n-butenes opens an additional pathway to carbon deposits.

1. Introduction

Isobutene is an important commodity chemical used as a feedstock for production of methyl-*tert*-butyl ether, methacrylate polymers, butyl rubber and polyisobutene. Commercial production of isobutene is based on steam cracking of naphtha and fluid catalytic cracking of high-boiling oil residues. However, market-driven demand rose interest in on-purpose production of this commodity thus placing non-oxidative dehydrogenation (DH) of isobutane to isobutene in focus as a prospective commercial process [1]. Despite the fact that several isobutane DH technologies employing $Pt–Sn/Al_2O_3$ or CrO_x/Al_2O_3 catalysts are successfully applied [1–3], improvements in terms of catalyst selectivity, on-stream stability, lifetime, environmental benignity and cost are still due.

The literature on non-oxidative isobutane DH catalysts beyond industrially applied $Pt–Sn/Al_2O_3$ and CrO_x/Al_2O_3 is sparse but some alternatives have been studied in the past [1]. $Ni/MgAl_2O_4$ showed ca. 70% selectivity to isobutene at isobutane conversion of only 3% [4]. Template-assisted co-condensation of Si and Ga precursors resulted in MCM-41-like mesoporous silica that produced isobutene with the selectivity of 80% at isobutane conversion below 10%, but only of 50% at the conversion of ca. 50% [5]. $VO_x/\gamma-Al_2O_3$ gave isobutene selectivity in the 80–90% range at isobutane conversion of 20–40% [6–8]. $VO_x/\theta-Al_2O_3$ was successfully applied in dehydrogenation of n-butane [9,10]. n-Butenes and butadiene were produced with an overall selectivity of 56% at n-butane conversion of 33% [9]. When using CO_2 as a weak oxidant, Shimada et al. [11] reported the selectivity to isobutene of 80% at isobutane conversion of 48% over FeO_x supported on activated carbon. Previously, we demonstrated that VO_x/MCM-41 prepared by grafting of vanadyl acetylacetonate ($VO(acac)_2$) onto MCM-41 silica was active and selective in isobutane [12] and propane [13] DH under O_2-lean conditions as well as in non-oxidative propane DH [14]. Extending this preparation method to aluminosilicate supports, we obtained catalysts with a space-time yield of propene only 25% lower than measured on the $Pt–Sn/Al_2O_3$ industrial analog [15].

Based on the above background, the aim of this study was to investigate the effects of the kind of VO_x species and of the supports on the catalytic performance (on-stream stability, activity and particularly selectivity) of $VO_x/SiO_2–Al_2O_3$ catalysts in non-oxidative DH of isobutane. To this end, supported VO_x species were formed via $VO(acac)_2$ grafting onto silica (MCM-41), aluminosilicate with the weight content of SiO_2 between 1 wt.% and 70 wt.% (Siral®) and alumina. In order to understand the role of secondary reactions, we also investigated activity and selectivity of the catalysts and the corresponding pristine supports in isobutene and 1-butene conversion. The distribution of VO_x species and acidic prop-

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* Corresponding authors.
E-mail addresses: uwe.rodemerck@catalysis.de (U. Rodemerck), evgenii.kondratenko@catalysis.de (E.V. Kondratenko).

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erties of the materials were elucidated by UV–vis and Raman spectroscopy as well as by infrared spectroscopy of adsorbed pyridine respectively. These characterization data were instrumental in establishing a correlation between structure and performance of the VO_x-based catalysts in isobutane DH. They also helped to explain the differences between isobutane and propane DH over the same type of catalysts tested in this study and in our previous study [15] respectively.

2. Experimental

2.1. Catalyst preparation

Silica (MCM-41), SiO_2–Al_2O_3 (Siral®, Sasol, SiO_2 content between 1 wt.% and 70 wt.%), and alumina (Chempur, Karlsruhe) were used as support materials. MCM-41 was synthesized following the procedure described in [16]. The catalysts were prepared by grafting $VO(acac)_2$ from a toluene solution onto supports as previously described [15]. Briefly, the dried support material was stirred in the toluene solution of $VO(acac)_2$ at room temperature for 24 h. After filtration, the solid was washed twice in pure toluene, dried at 80 °C for 20 h and calcined in static air at 550 °C for 12 h. To increase V loading, the above procedure was repeated. The obtained catalysts are abbreviated in the following text as V/Si, V/S1, V/S10, V/S40, V/S70 and V/Al, while the corresponding supports are denoted as SiO_2, S1, S10, S40, S70 and Al_2O_3. The numbers stand for the weight concentration of SiO_2 in SiO_2–Al_2O_3.

2.2. Catalyst characterization

The specific surface area (S_{BET}) of the supports and calcined catalysts was determined from N_2 adsorption isotherms measured at 77 K on BELSORP mini II (BEL, Japan) applying the Brunauer, Emmet and Teller (BET) equation for relative pressure range of $0.05 < p/p_0 < 0.30$. The obtained S_{BET} values are listed in Table 1.

The V content in the calcined catalysts (Table 1) was determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES) on Varian 715-ES.

To analyze the distribution of supported VO_x species, UV–vis measurements were performed at 550 °C in air that replicates the pretreatment applied prior to the catalytic experiments. A temperature-resistant UV–vis probe consisting of six radiating and one reading optical fibers was threaded through an oven's heating mantle and brought in contact with quartz reactor containing a catalyst. The spectra were collected in a diffusive reflectance mode on AVASPEC spectrometer equipped with DH-2000 deuterium-halogen light source (both from Avantes). $BaSO_4$ was used as a white standard. Kubelka–Munk function $F(R_\infty)$ was calculated from the reflectance R_∞ according to Eq. (1):

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty} \tag{1}$$

The surface acidity of the catalysts as well as of the pristine supports was assessed by infrared (IR) measurements of adsorbed pyridine using Tensor 27 spectrometer (Bruker) equipped with an in-house developed in situ cell. The sample powders were pressed into self-supporting wafers (50 mg, 20 mm in diameter). The samples were heated in synthetic air at 400 °C for 10 min, cooled to 25 °C and evacuated. Hereafter, pyridine was adsorbed until saturation was reached. Then the reaction cell was again evacuated to remove physisorbed pyridine. After heating in vacuum to 250 °C, the IR spectra of the adsorbed pyridine were recorded. Brønsted acidity and Lewis acidity were quantified by integrating the typical bands at 1540 cm^{-1} and 1450 cm^{-1}, respectively. Before IR tests with reduced catalysts, selected materials were treated in a flow of 5 vol.% H_2 in Ar at 550 °C for 6 h. After cooling down in the same gas mixture to room temperature the samples were transferred to the IR cell and again heated in a $H_2/He = 5/95$ mixture to 400 °C for 10 min followed by cooling to 25 °C and evacuation. Pyridine adsorption and IR measurement were carried out as described above for oxidized catalysts.

The Raman microspectroscopic investigations were performed on a Renishaw inVia Raman microscope equipped with a Linkam reaction cell. The ceramic reactor was filled with 40–50 mg of the catalyst. The samples were heated in He (50 ml/min) up to 250 °C with a heating rate of 20 K/min, where the Raman spectra were recorded. For the measurements a 442 nm laser was used with a laser power of 10% (Dual He/Cd Laser, 80/20 mW, objective 20×, acquisition time 10 s).

The redox behavior of oxidized VO_x species was analyzed by temperature-programmed reduction (TPR) in a setup containing eight individually heated continuous-flow fixed-bed reactors [17]. Fresh catalysts were heated in air at 550 °C for 2 h to oxidize VO_x species and to remove adsorbed water. After cooling to 50 °C in the same flow, they were flushed with Ar for 15 min and then heated in a flow of 5 vol.% H_2 in Ar at 10 K min^{-1} to the final tem-

Table 1
Selected physicochemical properties and catalytic results in isobutane DH of different catalysts and supports.

Catalyst or bare support	Notation	S_{BET} ($m^2\ g^{-1}$)	V loading (wt.%)	ωV[a] (V nm^{-2})	BA[b] (a.u.)	LA[b] (a.u.)	TOF[c] (s^{-1})
VO_x/SiO_2	V/Si	825	3.60	0.5	0.55	1.54	$9.0 \cdot 10^{-3}$
					0[e]	0.09[e]	
VO_x/Siral1	V/S1	238	4.10	2.0	0	3.88	$5.1 \cdot 10^{-3}$
VO_x/Siral10	V/S10	284	3.90	1.6	0.58	4.61	$4.9 \cdot 10^{-3}$
					0.57[e]	3.37[e]	
VO_x/Siral40	V/S40	249	2.96	1.0	1.79	3.78	$3.4 \cdot 10^{-3}$
VO_x/Siral70	V/S70	303	4.48	1.7	1.41	2.10	$3.4 \cdot 10^{-3}$
VO_x/Al_2O_3	V/Al	152	2.30	1.8	0	3.29	$5.3 \cdot 10^{-3}$
					0[e]	2.57[e]	
MCM-41	SiO_2	900	–	–	0	0	–
Siral1	S1	255	–	–	0	3.54	
Siral10	S10	350	–	–	Traces[d]	4.09	–
Siral40	S40	475	–	–	0.56	3.64	
Siral70	S70	360	–	–	0.49	1.55	
Al_2O_3	Al_2O_3	179	–	–	0	1.40	–

[a] Apparent surface density of vanadium atoms (ωV) was calculated from the weight metal concentration and catalyst specific surface area.

[b] Brønsted (BA) acidity and Lewis (LA) acidity were calculated from IR spectra of adsorbed pyridine recorded at 250 °C.

[c] Initial TOF calculated by Eqs. (5)–(7) from conversions given in Fig. 2 related to all vanadium contained in catalyst.

[d] Below 0.1.

[e] Reduced catalyst (6 h at 550 °C in 5% H_2/Ar).