Unmodified and MgO-modified monolayer V_2O_5-MoO_3/Al_2O_3 catalysts for propane oxidative dehydrogenation

Tamara Kharlamova,* Konstantin Timofeev, Valery Svetlichnyi, Olga Vodyankina
Tomsk State University, Tomsk, 634050, Russia
**Corresponding author: kharlamova83@gmail.com*

Abstract: The active species formation in unmodified and MgO-modified monolayer V_2O_5–MoO_3/Al_2O_3 catalysts as well as their composition and structure interrelation with catalytic properties towards propane ODH is considered. The samples prepared were characterized by nitrogen adsorption, STA, XRD, UV-vis DR, Raman spectroscopy, and H_2-TPR. The supported components in V_2O_5–MoO_3/Al_2O_3 catalysts are shown to interact with formation of $VMoO_x$ species or VO_x–MoO_x interfaces containing V–O–Mo bonds. The V_2O_5–MoO_3/Al_2O_3 samples modification by MgO leads to further changes in the composition and structure of active species. The effect of the species composition and structure on their redox potential and sample catalytic properties is discussed.

Keywords: Vanadium oxide catalysts, Supported multicomponent catalysts, Propane oxidative dehydrogenation.

1. Introduction

Vanadium oxide catalysts have been extensively studied as good candidates for oxidative dehydrogenation (ODH) of light alkanes. However, low selectivity of the catalysts remains a challenge for industrial implementation of ODH, especially that of propane. The idea to regulate the properties of vanadium oxide catalyst by changing the redox potential of vanadium oxide species via the formation of V–O–M bonds (M = Zr, Mo, Ti, Mg) has been repeatedly discussed. Typically, the systems of vanadium oxide–support or massive mixed oxides such as magnesium vanadates are considered. The effects of the component–component and/or component–support interactions in multicomponent MO_x–V_2O_5/support catalysts are poorly understood[1].

According to our recent studies on MgO–V_2O_5/Al_2O_3 materials, both Al^{3+} ions of oxide support (V–O–support bonds) and Mg^{2+} ions of the modifier introduced (V–O–Mg bonds) can act as ligands in the second coordination sphere of vanadium, changing the redox potential of surface vanadium oxide species[2, 3]. The method used for preparation of the multicomponent catalysts was shown to have a significant effect on the interaction between supported components and, thus, on the catalyst performances in ODH of propane[3].

The present paper is focused on formation of the active species in supported monolayer unmodified and MgO-modified V_2O_5–MoO_3/Al_2O_3 catalysts and the interrelation of their composition, structure and catalytic properties towards propane ODH.

2. Experimental

V_2O_5-MoO_3/Al_2O_3 catalysts were prepared by the incipient wetness impregnation of alumina support (γ-Al_2O_3, $S = 170\ m^2/g$, $V = 0.574\ cm^3/g$) with aqueous solutions of precursors of supported components. NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$ were used as parent substances of V and Mo, respectively. The total amount of V and Mo in the samples corresponded to a monolayer coverage. To increase the solubility of precursors in water and to provide high dispersion of supported phases, oxalic and citric acids were used. Both consecutive impregnation of the support by individual precursor solutions and combined impregnation by mixed precursor solution were used (Table). MgO-modified V_2O_5–MoO_3/Al_2O_3 catalysts were prepared by subsequent impregnation of V_2O_5–MoO_3/Al_2O_3 catalysts with aqueous solution of $Mg(NO_3)_2$. All samples prepared were calcined in air at 500°C.

Unmodified and MgO-modified V_2O_5–MoO_3/Al_2O_3 samples as well as intermediate V_2O_5/Al_2O_3 and MoO_3/Al_2O_3 systems were studied by a complex of methods including low-temperature nitrogen adsorption, XRD, UV-vis DR and Raman spectroscopy. The characteristics of the active species formation and distribution of the supported components in the V_2O_5–MoO_3/Al_2O_3, V_2O_5/Al_2O_3, and MoO_3/Al_2O_3 catalysts were additionally studied by STA of uncalcined samples and by benzaldehyde/ammonium titration of calcined samples. The redox properties of the samples were studied by temperature-programmed reduction by hydrogen (H_2-TPR). The catalytic properties of the samples were examined in the ODH of propane.

3. Results and discussion

According to analysis of the nitrogen adsorption data for the V_2O_5–MoO_3/Al_2O_3, V_2O_5/Al_2O_3, and MoO_3/Al_2O_3 samples, for all samples the change of textural characteristics in the course of vanadium and/or molybdenum oxide depositing corresponds to a uniform distribution of the supported components in the alumina support in the form of the oxide film or dispersed particles. XRD data indicate that the samples studied do not contain the crystalline phases of vanadium and molybdenum oxides.

Table. Some characteristics of V_2O_3/Al_2O_3, MoO_3/Al_2O_3, and V_2O_5-MoO_3/Al_2O_3 samples.

Sample	Preparation method	Content, wt. %		S, m^2/g	V, cm^3/g
		V_2O_5	MoO_3		
V_2O_3/Al_2O_3	impregnation	9.6	-	154	0.493
MoO_3/Al_2O_3	impregnation	-	10.4	164	0.495
V_2O_5–MoO_3/Al_2O_3(1)	consecutive impregnation: 1) V, 2) Mo	8.6	10.4	121	0.413
V_2O_5–MoO_3/Al_2O_3(2)	consecutive impregnation: 1) Mo, 2) V	9.6	9.4	119	0.402
V_2O_5–MoO_3/Al_2O_3(3)	combined impregnation	8.7	9.5	119	0.404

According to UV-vis DR and Raman spectroscopy data, the supported components are presented mainly as surface polymeric vanadium and molybdenum oxide species in V_2O_5/Al_2O_3 and MoO_3/Al_2O_3, respectively. The UV-vis DR spectra of all V_2O_5–MoO_3/Al_2O_3 catalysts are identical and primarily caused by the presence of surface polymeric vanadium oxide species without detectable spectral contribution from molybdenum oxide species. However, the presence of molybdenum leads to an increase in the absorption intensity at ~400 nm in the spectra in comparison with the one of the V_2O_5/Al_2O_3 sample. This indirectly indicates the influence of molybdenum on the structure and electronic configuration of surface vanadium-oxide species. The presence of bands at 231, 770 and 1010 cm^{-1} in Raman spectra of the V_2O_5–MoO_3/Al_2O_3 samples additionally confirms the formation of V-O-Mo bonds in these systems. These bonds are presented in $VMoO_x$ species or at the interfaces of VO_x and MoO_x species depending on the preparation approach used.

The modification of the samples by MgO leads to further changes in the composition and structure of the surface species in supported monolayer V_2O_5–MoO_3/Al_2O_3 catalysts due to formation of V–O–Mg and Mo–O–Mg bonds.

4. Conclusions

The composition and structure of the surface species formed in the V_2O_5–MoO_3/Al_2O_3 and MgO–V_2O_5–MoO_3/Al_2O_3 catalysts were studied. The interaction of supported components to form $VMoO_x$ species or VO_x–MoO_x interfaces containing V–O–Mo bonds was revealed in the V_2O_5–MoO_3/Al_2O_3 catalyst. The further changes in the composition and structure of the surface species are observed in MgO-modified V_2O_5–MoO_3/Al_2O_3 catalysts. The effect of composition and structural features of surface species formed in V_2O_5–MoO_3/Al_2O_3 and MgO–V_2O_5–MoO_3/Al_2O_3 catalysts on their reactivity and catalytic properties are discussed in details.

References

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