Research Article

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Synthesis, properties, and activity of MoVTaNbO catalysts modified by zirconia-pillared clays in oxidative dehydrogenation of ethane

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Abstract: Composites comprising MoVTaNbO mixed oxide and zirconia-pillared montmorillonite clays (PilCs) were prepared. XRD and TEM with EDX studies confirmed the preservation of M1 MoVTaNbO phase in these composites responsible for high activity and selectivity in ethane oxidative dehydrogenation into ethylene. For composites with PilC content of 10 wt%, the best ethylene yield exceeding that of bulk MoVTaNbO oxide was demonstrated for clays with zirconia pillars doped with Ce and Al possessing the highest specific surface area. This is explained by optimized chemical interaction of these clays with MoVTaNbO mixed oxide improving its bulk oxygen mobility and reactivity by structure disordering while blocking surface sites responsible for combustion due to the stabilization of the reactive terminal oxygen species.

Keywords: oxidative dehydrogenation of ethane to ethylene, MoVTaNbO mixed oxide, composites with pillared clays

1 Introduction

Oxidative dehydrogenation of ethane (ODE) is a perspective method for ethylene production, since this method allows the process to be carried out at relatively low temperatures with sufficiently high selectivity [1]. Currently, the most effective catalysts for this process are considered to be MoVTaNbO mixed oxides [2–6]. The active and selective phase of the MoVTaNbO catalyst denoted by M1 with the composition $(AO)_{2-2x}(A_2O)_xM_{20}O_{56}$ ($0 \leq x \leq 1$, A = Te, Sb, and M = Mo, V, and Nb) has the orthorhombic structure [7]. Botella et al. [8] demonstrated successful design of MoVTaNbO catalyst with a high activity and selectivity in the ODE (80% ethylene selectivity at 340–400°C). However, attempts to increase activity and selectivity of these catalysts continue. Modifying cationic composition of the M1 phase does not lead to a significant increase in activity. In addition, MoVTaNb mixed oxides have a low specific surface area, which limits their potential opportunities for industrial application. Traditional approach to enhance the surface area of the catalysts is based on the use of supports with a high surface area, which allows to disperse the active component particles, thus increasing the surface to volume ratio and, therefore, the amount of accessible active sites on the surface. Using various supports like alumina, silica, TiO_2 , or Nb_2O_5 for preparation of high surface area MoVTaNbO-based catalysts failed since supporting appeared to strongly inhibit the crystallization of the M1 phase [9,10]. Nanocomposite oxide catalysts of the overall composition $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}/n\ SiO_2$ ($n = 0, 10, 25, 35$, and 50 wt%) were tested in ODE [11]. The catalyst with 10 wt%

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SiO₂ content exhibits the highest specific (per gram) activity due to the presence of nanodomains of the M1 phase. This implies that a promising approach to enhance the performance of these mixed oxide catalysts could be based on adding a moderate amount of promoters with a high dispersion, thus forming nanocomposites with improved textural characteristics. At higher SiO₂ content, the activity declines due to the segregation of amorphous SiO₂ layers on the catalysts surface. To deal with this problem, Bondareva et al. [12] prepared MoVTenbO composites with Al–Si–O oxide (SiO₂ content 5 wt%) with a support content up to 70%. Again, the highest activity and ethylene selectivity were observed for the catalyst with the additive content of 10 wt% due to the formation of mixed Al-containing phases at a higher support content. Hence, more chemically stable high surface area supports are apparently required to provide a higher dispersion of MoVTenbO oxide without deteriorating its performance.

Pillared clays containing in their interlayer space ZrO₂, CeO₂, La₂O₃, and other oxide nanoparticles are promising as supports for catalysts of different catalytic processes. These materials possess a high thermal stability and a developed pore structure comprising micropores (corresponding to galleries between aluminosilicate layers) and mesopores (generated due to faults in the clay sheets' stacking). Besides, clays constitute good and cheap supports to achieve high dispersion of metal oxide species [13–17].

In this article, we describe the characterization and catalytic performance in ODE of nanocomposites comprising Mo–V–Nb–Te mixed oxides with zirconia-pillared clays (Zr-PilCs) synthesized using natural clays of Kazakhstan's fields [14–16]. Features of interaction between the components during the catalyst preparation affecting their texture, structural features, and reactivity were elucidated by N₂ adsorption, XRD, and HRTEM with EDX. Since for composites with PilCs, the best performance was also revealed with additive content of 10 wt%, and the main attention was devoted to the elucidating effect of cations modifying zirconia nanopillars at PilC preparation, and, hence, their textural features, on the composite's characteristics and catalytic properties at this fixed content of PilCs.

2 Methods

2.1 PilC preparation

Synthesis of PilCs samples has been carried out using a montmorillonite (MM) clay, where initial CaO and MgO contents are of ~2 wt% and Fe₂O₃ admixture content is of 4.4 wt% (Table 1) according to the optimized procedures of pillaring with Zr–O polynuclear species doped with Ce, Ca, Al, and Ba cations described in details elsewhere [14–16]. Zr-containing solutions (Zr concentration 0.2 M) were prepared from recrystallized ZrOCl₂·8H₂O (Vekton, Russia) and zirconium acetate (solution in diluted acetic acid; Aldrich, Germany). After the pillaring and washing procedures, the obtained PilC was dried for 24 h at room temperature and then calcined at 500°C for 5 h.

2.2 Catalyst preparation

The oxide catalysts of the atomic composition V:Mo:Te:Nb = 0.3:1:0.23:0.12 were synthesized by the procedure described in [18] for the bulk samples. The starting chemicals were ammonium molybdate (NH₄)₆Mo₇O₂₄·4H₂O (Vekton, Russia), ammonium metavanadate NH₄VO₃ (Reakhim, Russia), telluric acid H₆TeO₆ (Alfa Aesar, Germany), and niobium oxalate solution (C₂O₄²⁻/Nb = 3.0) freshly prepared by mixing a precipitated niobium hydroxide in an oxalic acid solution. Niobium hydroxide was obtained by the precipitation of NbCl₅ (Acros Organics) with an aqueous solution of ammonia (Acros) at pH 7. The main substance content of the chemicals was higher than 99%. To a VMoTe solution prepared by dissolving the starting compounds, a solution of niobium oxalate and nitric acid was added in succession providing pH 3. To prepare bulk mixed oxide, this solution was fast dried using a laboratory dryer (BUCHI B-29, Germany) with an inlet temperature of 220°C and an outlet temperature of 110°C, then pelletized followed by crushing and milling of pellets, and the 0.25–0.5 mm fraction was separated by sieving. It was then subjected to a short heat treatment at 310°C in air and calcined in the He flow at 550°C for 2 h.

Table 1: Elemental analysis of the initial sample of montmorillonite

Sample	Content, wt%									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Others
Initial clay	55.5	19.38	4.4	0.3	1.98	2.18	0.2	0.5	0.14	11.3

The MoVTenbO/PILC catalysts were prepared by adding the necessary amount of PilCs (mainly 10 wt% as related to oxide) into the mixed solution described above. The obtained composites were subjected to the same thermal procedures described above for the bulk sample.

2.3 Characterization

Structural and textural properties of materials were studied by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) with elemental analysis (EDX), and N₂ adsorption. For XRD studies, a D8 Advance (Bruker, Germany) diffractometer with Cu-K α radiation and LynxEye position sensitive detector was used (2θ range 20–85°, step size 0.05, and accumulation time 3 s).

For HRTEM studies, a JEM-2200FS (JEOL Ltd., Japan; acceleration voltage 200 kV, lattice resolution 1 Å, and Cs-corrector) equipped with an EDX spectrometer (JEOL Ltd., Japan) and a JEM-2010 (JEOL Ltd.; accelerating voltage 200 kV, lattice resolution 1.4 Å) instruments were used. Samples for these studies were prepared by ultrasonic dispersing in ethanol followed by suspension deposition onto a holey carbon film located on a copper grid.

In textural studies, N₂ adsorption isotherms [–196°C, an ASAP-2400 (Micromeritics, USA)] were obtained for samples pretreated in vacuum (150°C, 16 h). T-plot analysis was used to determine the micropore volume and the average pore size was estimated as 4 V/A. The four-point Brunauer-Emmet-Teller (BET) method (a SORBI N.4.1 apparatus, samples pretreatment in vacuum at 200°C for 1 h) was used to determine their specific surface area.

Temperature-programmed reduction by hydrogen (H₂-TPR) was carried out in a flow installation (10 vol% H₂ in Ar, flow rate 40 mL/min) [19].

2.4 Catalytic reaction

The catalytic properties were investigated in a setup with online chromatographic analysis of the reaction mixture components described in [11,12,18,19]. Experiments were carried out at atmospheric pressure in a tubular reactor with coaxially located thermocouple pocket in a fixed bed of the catalyst. The feed composition was C₂H₆:O₂:N₂ = 10:10:80 (vol%) with the reaction *T* of 400–470°C and GHSV of 600–2,400 h^{–1}. The catalyst fraction was 0.25–0.50 mm. Controlled experiment conducted at 480°C confirmed the absence of transformations of both ethane and oxygen in empty reactor without catalyst.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Textural properties

Table 2 presents the textural characteristics of PilCs used for synthesis of composites. Both specific surface area and pore volume vary substantially depending upon the nature of the pillaring species but micropore share being negligible. This is determined by the effect of the composition and aging conditions of pillaring species on their shape and size as considered in original publications [14–16]. Smaller size of pillaring species results in smaller pore size (distance between aluminosilicate layers) and larger values of specific surface area.

Table 3 presents information about specific surface area of bulk VMoTeNbO catalyst and composites with 10 wt% of PilCs. In agreement with earlier obtained results of adding close amounts of silica and Al–Si–O to this mixed oxide [11,12], specific surface area increases only slightly for composites with this content of PilC.

Table 2: Textural characteristics of pillared clays

No.	Abbreviation, type, and content of pillars	S_{BET} , m ² /g	V_{pores} , cm ³ /g	$V_{\text{micropore}}$, cm ³ /g	Average pore diameter, Å	D_{pores} , Å
1	Montmorillonite clay (MM)	54	0.12	0.002	95	139
2	Zr–Ba-pillared MM, 20 wt% ZrO ₂ + 0.2% Ba	100	0.20	0	86	138
3	Al-pillared MM, 4.0 wt% Al	40	0.17	0	176	204
4	Zr–Ca-pillared MM, 20 wt% ZrO ₂ + 0.2 wt% Ca	67	0.12	0	77	128
5	Zr–Ce-pillared MM, 20 wt% ZrO ₂ + 0.06 wt% Ce	217	0.06	0	24	106
6	Zr–Al-pillared MM, 20 wt% ZrO ₂ + 4.8 wt% Al	230	0.07	0.060	26	95

Table 3: Specific surface area of catalysts

Sample	$S_{sp.}, m^2/g$
Bulk MoVTenbO	5.0
MoVTenbO + Zr-Ce-PilC	5.7
MoVTenbO + Zr-Al-PilC	6.1

Apparently at a high content of added PilCs, the specific surface area of composites will also increase following earlier observed trends [11,12]: up to 20–30 m²/g at additive content of up to 50 wt%.

3.2 Structural characteristics

According to the X-ray data (Figure 1), the main phase of PilCs is disordered dehydrated montmorillonite. For all samples after calcination at 500°C, the interlayer (001) reflex situated for pure montmorillonite at ~5° is not observed due to disordering by the intercalated zirconia nanoparticles. In addition to the main phase of MM (PDF 00-001-0026), reflections of quartz (a natural admixture in montmorillonite) and zirconium oxide of monoclinic and tetragonal modification (related to aggregated pillaring species) are also observed.

Figure 2 presents the diffraction patterns of bulk VMoTeNbO oxide and its composites with 10 wt% of Zr-Ce- or Zr-Al-PilCs. MoVTenbO catalyst is rather a pure M1 phase (active component in oxidative dehydrogenation of alkanes) [2–8,18] with a minor admixture of M2 phase. Its diffraction pattern is in good agreement

Figure 1: Diffraction patterns of Zr-Ce-, Zr-Al-, and Zr-Al-pillared clays.

with the calculated X-ray pattern for the M1 phase presented in [20]. For these composites, the phase composition of VMoTeNbO oxide is the same as that of pure bulk oxide comprising the mixture of M1 phase and M2 phase in ~9:1 ratio. In the diffraction patterns of composites, peaks corresponding to M1 phase (PDF 00-058-0789) and M2 phase (PDF 00-057-1099) are identical to those in MoVTenbO prototype [4,6]. No other impurity phases were observed, which shows that the prepared complex oxides exhibit high M1 phase purity. Main reflections corresponding to the montmorillonite phase are absent, which agrees with a small amount of added PilCs. Hence, the addition of PilCs to mixed MoVTenbO oxide has not resulted in its destruction or modification of its phase composition.

According to the XRD data (Figure 3), the structure of M1 and M2 phases in composites is maintained after catalytic investigations. Other oxide V-Mo phases were not detected.

Figures 4–7 present the results of high-resolution TEM studies of bulk MoVTenbO oxide and its composite with 10 wt% of Zr-Ce-PilC before and after testing in reaction. For bulk oxide before and after reaction point microdiffraction data confirmed the coexistence of regions corresponding to orthorhombic M1 phase (TeO) M₅O₁₄ (M = Mo, V, and Nb) with P6₃ space group (Figures 4c, 5b, and c) and pseudo hexagonal M2 phase

Figure 2: Diffraction patterns of bulk VMoTeNbO and its composites with 10 wt% of Zr-Ce- or Zr-Al-pillared clays.

Figure 3: Diffraction patterns of bulk VMoTeNbO and its composites with 10 wt% of Zr–Ce- or Zr–Al-pillared clays after catalytic tests.

(Figure 4b) (TeO) M_3O_9 ($M = Mo, V, \text{ and } Nb$) with $Pmm2$ space group [2,4,6,20]. Moreover, domains of Mo–V–O [($Mo_{0.3}V_{0.7}$) $_2O_5$ (PDF#21-576) and $V_{0.95}Mo_{0.97}O_5$ (PDF#77-649)] are observed as well (Figure 4d).

For MoVTNbO catalyst, after reaction (Figure 5) the particles' morphology and crystallinity remain unchanged.

For composite catalysts, the most important feature is that in some regions, the surface layer is enriched by either Si or Al cations (Figures 6b and 7c) apparently leached from particles of PiICs at the stage of evaporation of their suspension in strongly acidic solution. Moreover, in Figure 6b a region comprising stacked amorphous silica nanoparticles with MoVTNbO clusters was observed, resembling similar features revealed for composites with a high silica content [11]. Since particles of PiICs were not observed in all cases, this implies that in strongly acidic solution at the stage of evaporation, the PiICs could be completely disintegrated into nanosheets of silica and clusters of zirconia while all other cations were transferred into solution incorporating

Figure 4: TEM image morphology (a), HRTEM and FFT images with labeled observed interplanar distances and corresponding indexes for phases M2 (b), M1 (c), and Mo–V–O (d) of MoVTNbO catalyst before reaction.

Figure 5: TEM image morphology (a), HRTEM and FFT images with labeled observed interplanar distances and corresponding indexes for phases M1 (b and c) and Mo-V-O (d) of MoVTenbO catalyst after reaction.

into the surface layers/bulk of MoVTenbO particles after calcinations.

Figure 7 presents TEM images and EDX data for MoV-TenbO + Zr-Ce-PilC catalyst after reaction. As follows from these data, main structural features of catalyst remained unchanged after reaction.

3.3 Samples reactivity by H₂-TPR

As follows from H₂-TPR curves shown in Figure 8, for both composites with 10 wt% of Zr-Ce or Zr-Al, the PilCs reduction peaks are shifted to lower temperatures as compared with bulk oxide, while amounts of removed oxygen increase as well (Table 3), thus demonstrating increase in complex oxide reactivity due to the incorporation of PilC. By position, these TPR peaks correspond to

the removal of strongly bound surface/lattice oxygen species [6]. In addition, the appearance of new peaks in the high temperature range 763 and 844°C implies much stronger interaction of catalyst cations with nanosized zirconia and silica particles and, hence, much higher oxygen bonding strength. Note that for PilCs, reactivity is much lower (see inset in Figure 8) as expected, so their share could not be revealed at all. Hence, the increase in reactivity can only be explained by disordering of MoVTenbO particles in composites due to incorporation of cations leached from Zr-PilC, thus generating point and extended defects, which facilitate oxygen migration from the bulk. Note that for M1 phase comprising nanoparticles high-temperature H₂-TPR peaks were not observed at all [6]. Such disordering can also increase surface reactivity of composites. Very important point is that for composites, any new low-temperature peaks have

Figure 6: TEM images and EDX data for MoVTenbO + Zr-Ce-PiIC catalyst before reaction. (a) general morphology and (b–d) selected areas for elemental analysis.

not appeared, hence, weakly bound reactive oxygen forms, which could be responsible for ethane and ethylene combustion, have not emerged (Table 4).

3.4 Catalytic properties

To check the effect of the PiIC content in composite on its catalytic properties, for Al-PiIC additive (selected as the most neutral one), its content was varied from 7 to 25 wt%. As follows from Figure S1, the increase in additive content has resulted in decrease in activity, while ethylene selectivity varied only slightly, following earlier obtained

trends for such additives as SiO₂ and Al-Si-O [11,12]. Hence, in a similar way, it can be explained by blocking the surface sites of M1 phase particles by amorphous Al-Si-O clusters/layers and/or by the formation of aluminum molybdate Al₂(MoO₄)₃ clusters destroying the surface planes of active M1 phase. This demonstrates that for PiICs as additives, the problem of strong interaction with MoVTenbO oxide revealed by TEM with EDX remains crucial, which justifies our selection for studies of composites with fixed additive level of 10 wt%.

For studied samples' data on dependence of ethane conversion and ethylene/CO_x selectivity on contact time and temperature are provided in Table S1. Figure 9

Figure 7: TEM images and EDX data for MoVTenbO + Zr-Ce-PiIC catalyst after reaction. (a) General morphology and (b–d) selected areas for elemental analysis.

compares the results for bulk MoVTenbO oxide and the most active and the least active composites.

Comparison with the textural characteristics (Table 2) shows that the most active composites have PiIC additives with the highest specific surface area. This implies that the most important factor determining composites' catalytic performance could be chemical interaction between their components at the preparation stage, which apparently proceeds easier for dopants with a higher specific surface area. Note that for the most active composites, ethane conversions practically coincide with those for bulk MoVTenbO oxide (Figure 9a). In this case,

three effects of doping appear to compensate each other – while surface disordering due to doping increases its reactivity (Figure 8), and specific surface area increases with doping as well (Table 3); some blocking of surface sites by nonreactive Zr–O and Al–O complexes could occur. As a result, ethane conversion could not be changed by doping with 10 wt% of Zr–Ce- and Zr–Al-PiIC. For catalysts doped with Zr–Ca or Zr–Ba PiIC, a lower activity (Table S1, Figure 9a) can be explained by partial blocking of surface sites by segregated nonreducible Ca and Ba cations as well as by carbonates bound with them. For these least active composites, a higher

Figure 8: H₂-TPR curves for bulk PilC, MoVTeNbO oxide, and its composites with 10 wt% of pillared clays.

Table 4: Characteristics of H₂-TPR spectra

No	Sample	The maxima of peaks, °C			H ₂ consumption, mol H ₂ g ⁻¹
		T ₁	T ₂	T ₃	
1	MoVTeNbO	555	—	850	0.013
2	MoVTeNbO + 10 wt% Zr–Ce–PilC	549	—	857	0.016
3	MoVTeNbO + 10 wt% Zr–Al–PilC	532	763	844	0.017

Figure 9: Comparison of C₂H₆ conversion (a) and ethylene selectivity (b) dependence on temperature at contact time 5.52 s for bulk MoVTeNbO oxide and its composites with 10 wt% of Zr–Ce-, Zr–Al-, and Zr–Ca-PilCs.

ethylene selectivity in all studied temperature range correlates with lower ethane conversions (Table S1, Figure 9). Note that for the case of pure montmorillonite as dopant (Table S1), ethane conversion and ethylene selectivity are also lower than for pure MoVTeNbO oxide being close to those for catalysts doped with Zr–Ca- or Zr–Ba-PilC. Since pure montmorillonite contains ~2 wt% CaO as well as ~2 wt% MgO (Table 1), this negative effect of doping can also be explained by the negative effect of the surface site blocking by carbonates bound with these basic cations, which are apparently stable in the studied moderate temperature range. In the case of Zr–Ce- and Zr–Al-PilCs, more acidic Zr, Ce, and Al cations could not stabilize carbonates in this temperature range, so their effect on blocking surface sites is not so substantial.

On the other hand, ethylene selectivity was somewhat improved due to doping with Zr–Al-PilC (Figure S2), which can be explained by some decrease in the surface coverage by the terminal oxygen species responsible for ethylene combustion. Moreover, for samples doped with Zr–Ce- and Zr–Al-PilC, ethylene selectivity also tends to be higher than that for undoped sample at temperatures >400°C (Figure 9), providing a higher ethylene yield, which is important for practice. Hence, a higher reactivity of these composites revealed by H₂-TPR has not resulted in a lower ethylene selectivity. Since ethylene deep oxidation is related to more reactive terminal Me–O oxygen species [21,22], it implies that incorporation of Ce, Zr, and Al cations into the surface layer of M1 particles has not resulted in the generation of such species, which agrees with the absence of any new low-temperature H₂-TPR peaks (Figure 8). Moreover, these cations could block surface sites on the faces of M1 phase, where oxygen adsorption in reaction conditions generates terminal M–O oxygen species.

As follows from Figure S2, at 400°C the dependence of ethylene selectivity on ethane conversion for doped

samples excluding only that doped with Zr–Al–PilC is fitted by the same line. Although for the latter sample, the difference with other samples is not big, it appears to correlate with slightly higher reactivity and amount of oxygen removed in H_2 -TPR (Table 3). Since Al cations are contained both in pillars and in aluminosilicate clay layers, their surface content in doped MoVTenbO samples revealed by EDX (Figures 6 and 7) is higher than that of Zr and Ce, so they are expected to play a substantial role in the surface disordering. Note that addition of up to 25 wt% of Al–Si–O support to MoVTenbO oxide has not affected the dependence of ethylene selectivity on ethane conversion at all [12]. This apparently demonstrates specificity of interaction of MoVTenbO oxide with Zr–PilCs.

From the fundamental point of view, identical temperature dependencies of ethane conversion and ethylene selectivity for composites with Zr–Ce and Zr–Al PilC additives (Figure 9) imply the absence of any synergistic action of Ce cation able to change its oxidation stage, which can be explained by a complex composition, structure, and redox properties of M1 MoVTenbO oxide phase determining its high performance in the studied reaction [1–12,21,22]. Hence, the increase of the specific surface area, generation of point and extended defects due to incorporation of Zr, Ce, and Al cations onto MoVTenbO lattice, some surface structure disordering and blocking of sites able to retain terminal oxygen forms responsible for combustion appear to provide a better performance of catalysts doped with Zr–Ce and Zr–Al PilC. Detailed characterization of the defect and surface structure of these nanocomposites by applying modern spectroscopic methods is outside the scope of this article and could be the subject of the future studies.

From the practical point of view, the best composites of MoVTenbO oxide with PilCs provide at 400°C ethane conversion and ethylene selectivity close to those of the best composites with SiO_2 and Al–Si–O additives having close specific surface areas as well [11,12]. To achieve a higher performance of composites with PilC additives, the content of additives is to be increased while keeping chemical interaction between components at optimized level. It might be achieved by varying preparation conditions and adding PilCs not directly into the mixed acid solution of salts but to products of their evaporation ultrasonically dispersed in some solvents or subjected to hydrothermal treatment [10], which is certainly the subject of the future studies.

4 Conclusion

Composites comprising MoVTenbO mixed oxide and zirconia-pillared montmorillonite clay additives were prepared by a simple procedure of evaporation of clay suspension in mixed salt solution followed by calcination. XRD and TEM with EDX studies confirmed the preservation of M1 phase in these composites responsible for high activity and selectivity in ethane oxidative dehydrogenation to ethylene despite strong chemical interaction between the components. The best catalytic properties (ethane conversion being equal to that for undoped MoVTenbO oxide with a higher ethylene selectivity) were demonstrated for composites with additive content of 10 wt% and zirconia pillars doped with Ce and Al. This is explained by optimized chemical interaction of additives with MoVTenbO mixed oxide, improving its bulk oxygen mobility and reactivity by some structure disordering and blocking surface sites stabilizing terminal M–O oxygen species responsible for combustion.

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