Novel Mesoporous Mixed Nb-M (M = V, Mo, and Sb) Oxides for Oxidative Dehydrogenation of Propane

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Novel thermally stable mesoporous mixed metal Nb–M (M = V, Mo and Sb) oxides were synthesized in the presence of a nonionic Pluronic P123 surfactant. These oxides displayed promising pore structures and chemical compositions for selective oxidative functionalization of propane: high surface areas (up to 200 m²/g), large pore sizes (5–14 nm), and high pore volumes (up to 0.46 cm³/g). The oxidative dehydrogenation of propane to propylene over mesoporous mixed metal Nb–M oxides employed as a probe reaction suggested that the M component was dispersed as the molecular surface species and also formed a solid solution with NbO_x in the inorganic walls of these mesoporous mixed metal oxides.

Introduction

The discovery of M41S silicate materials ushered in a new era in the synthesis of ordered mesoporous materials and inspired the search for structurally similar phases with non-silicate compositions. In particular, the mixed oxides of vanadium, molybdenum, antimony, and niobium are highly promising as selective (amm)oxidation catalysts of lower alkanes, such as propane.^{1,2,3-6} Although the binary mesostructured oxides of vanadium, molybdenum and niobium have been reported,⁷ only mesostructured niobium oxides are thermally stable at typical temperatures employed for vapor-phase alkane (amm)oxidation (>300 °C). The majority of such mesostructured transition metal oxides with chemical compositions promising for selective alkane (amm)oxidation reactions reported to date suffered from limited thermal stability. Incomplete cross-linking of the inorganic frameworks, strong covalent bonds between the inorganic species and surfactant molecules, and low Tammann temperature of the constituent metal oxides are among the most notable causes of the limited thermal stability of mesoporous binary and mixed metal oxides.8

We report here novel thermally stable mesoporous Nb–M (M = V, Mo, and Sb) mixed metal oxides synthesized by evaporation-induced self-assembly (EISA)⁹ employing Nb oxide possessing a high Tammann temperature as a major structural component. These mixed metal oxide phases displayed good thermal stability (400 °C), large pore sizes (5–14 nm), high surface areas (up to 200 m²/g), and flexible inorganic wall compositions. The catalytic roles of the constituent metal oxides were investigated in oxidative dehydrogenation of propane

(ODH), which represents the first step in propane ammoxidation to acrylonitrile and oxidation to acrylic acid.

Experimental Section

Synthesis of Mesoporous Mixed Metal Oxides. Triblock copolymer surfactant (HO(CH₂CH₂O)₂₀(CH₂CH(CH₃O)₇₀(CH₂-CH₂O)₂₀H designated as $EO_{20}PO_{70}EO_{20}$, Pluronic P123; average molecular weight = 5800), anhydrous niobium chloride (99%), vanadium pentoxide (99.6%), vanadium(IV) sulfate (99.9%), molybdenum trioxide (99.5%), antimonous oxide (99.9%) (Alfa Aesar), and ethanol (for industrial use, AAPER Alcohol and Chemical Co.) were used as received.

A mesoporous mixed Nb–M (M = Mo, V, and Sb) oxides were prepared by evaporation-induced-self-assembly (EISA). In a typical synthesis, 1 g of $EO_{20}PO_{70}EO_{20}$ was dissolved in 10 mL of ethanol. Then, 0.01 mol NbCl₅ was added to the surfactant solution under vigorous stirring for 0.5 h. The M oxide sources, e.g., V(V), V(IV) or Sb(III) at M/Nb = 0.3 or Mo(VI) at Mo(VI)/Nb = 0.1, were added to 2.7–3.6 g of concentrated HCl solution at pH = 1–2 and then mixed with 5–10 mL of ethanol. The M oxide containing solution was added to the Nb– surfactant solution under stirring. The resulting sol solution was gelled in an open Petri dish at 50 °C in air at 18% relative humidity for 2–5 days. The as-synthesized samples were calcined at 400–600 °C for 3–5 h in air to remove the surfactant.

Structural Characterization. Small-angle X-ray scattering (SAXS) patterns were collected using Rigaku RU–V 200 model and Cu K α radiation. X-ray diffraction (XRD) patterns were obtained using Siemens D-500 diffractometer with Cu K α radiation and a step size of 0.02°/s. The N₂ adsorption– desorption isotherms were measured at 77 K using Micromeritics Tri-Star 3000 porosimeter. The pore size distributions and surface areas were determined by the Barrett–Joyner–Halenda (BJH)¹⁰ and Brunauer–Emmett–Teller (BET)¹¹ methods, respectively. The pore volumes were calculated by the BJH method. Transmission electron microscopy (TEM) studies were

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TABLE 1: Selected Characteristics of Mesoporous Mixed Nb–V–O, Nb–Mo–O, and Nb–Sb–O Phases Calcined at 400 °C, Where $T_{\text{aging}} = \text{Aging Time}$, $S_{\text{BET}} = \text{BET}$ Surface Area, $V_{\text{P}} = \text{BJH}$ Pore Volume, and D = BJH Pore Size

sample	precursor	ICP composition	T_{aging} (day)	pH/H ₂ O (unitless/g)	$S_{\rm BET}$ (m ² /g)	$V_{\rm P}$ (cm ³ /g)	D (nm)	$S_{\text{Theory}} \ (\mathrm{m}^2/\mathrm{g})^a$
Nb-V-O-2	V_2O_5	$V_{0.079}Nb_{0.264}O_x^{\ b}$	3	1.1/2.7	139	0.33	11	120
Nb-V-O-2'	V_2O_5	V _{0.076} Nb _{0.245} O _x ^b	5	1.1/2.7	159	0.33	9	147
Nb-V-O-3	V_2O_5		3	2.2/3.6	125	0.32	13	98
Nb-V-O-3'	V_2O_5		5	2.2/3.6	155	0.38	12.5	122
Nb-V-O-4	V_2O_5		3	1.1/3.6	155	0.33	11	120
Nb-V-O-4'	V_2O_5		5	1.1/3.6	223	0.39	9.5	164
Nb-V-O-5	$VOSO_4$	$V_{0.041}Nb_{0.073}O_x^{\ b}$	2	0.8/1.8	197	0.46	9.5	194
Nb-V-O-6	$VOSO_4$		2	1.08/1.8	144	0.42	15	112
Nb-V-O-7	$VOSO_4$		2	0.8/2.7	161	0.41	14.2	126
Nb-V-O-8	$VOSO_4$		2	1.08/1.08	182	0.44	11.7	176
Nb-Mo-O-1	MoO_3	$Mo_{0.031}Nb_{0.307}O_x^{b}$	2	1.1/1.8	159	0.24	6.4	150
Nb-Mo-O-4	MoO_3		2	1.1/2.7	111	0.18	14	51
Nb-Sb-O-1	Sb_2O_5		2		142	0.18	5.5	131
Nb-Sb-O-2	Sb_2O_5		2	1.1/1.8	160	0.17	4.6	148
Nb-Sb-O-3	Sb_2O_5		2	2.2/1.8	174	022	6.5	135
Nb-Sb-O-4	Sb_2O_5	Sb _{0.54} Nb _{1.52} O _x ^b	2	-/1.8	197	0.22	4.9	180

^{*a*} Assuming uniform and cylindrical pores, $S_{\text{Theory}} = 4V/D$ (V = pore volume; D = pore size). ^{*b*} Samples selected for the structural and reactivity characterization.

carried out on a Philips CM-20 electron microscope operating at 200 kV. The samples for TEM were prepared by depositing the powders suspended in ethanol onto the TEM Ni grids. The ambient Raman spectra were obtained with the 514 nm line of an Ar^+ ion laser. The exciting laser power was measured at the sample to be about 5 mW. The scattered radiation was analyzed using a model T-64000 Triple monochromator system (Jobin Yvon Inc.) equipped with a charge coupled device detector and a microscope attachment.

Propane ODH. Propane ODH was performed using a fixedbed microreactor loaded with 0.2 g of 0.3-0.6 mm diameter catalyst particles. The axial temperature profile was monitored by a thermocouple placed inside the catalytic bed. The feed employed was 9% O₂, 29% propane, and the balance helium flowing at 25 mL min⁻¹. The reactants and products were analyzed by GC (HP-5860 model) equipped with flame ionization and thermal-conductivity detectors. The carbon balances agreed within 5 mol. %.

Results and Discussion

Effect of Synthesis Conditions. Selected synthesis parameters and structural properties of the mesoporous mixed metal oxides obtained in this study are shown in Table 1. Physicochemical properties and thermal stabilities of mesoporous transition metal oxides are influenced dramatically by the synthesis conditions. They can be divided into two classes: (1) chemical factors related to surfactants, inorganic precursors, and the rates of hydrolysis and condensation reactions; (2) processing conditions that govern the diffusion of volatile EtOH, H₂O, and HCl to or from the mesostructured phase.12 The interactions between inorganic species and surfactant arrays are crucial for the resultant structural order of mesoporous materials. These interactions are affected by such characteristics of the selfassembly process as the rate of hydrolysis and condensation, the degree of condensation and resultant cross-linking of inorganic oxide species. The causes of limited thermal stability of (mixed) transition metal oxides have been recently reviewed.8 Some of them relate to the control over these parameters, such as the charge matching and the strength of the interactions between inorganic species and surfactants that are discussed below.

To favor fast hydrolysis and slow condensation of metal oxide sources promoting the formation of small oligomers, the synthesis pH was kept close to the isoelectric point of niobium and vanadium hydroxo species (pH = $\sim 1-2$), while the hydrolysis ratio ($h = H_2O/Nb$) was fixed at 10-20. The presence of water plays a role in influencing the evaporation rates of EtOH and HCl as well as the polarity of the medium which is a key factor in the formation of surfactant micelles and their organization.13 In situ 2D-SAXS13 and interferometry data indicated that template nanosegregation is mainly governed by the atmospheric relative humidity (RH), which controls the water evaporation from the sol solution. Most mesoporous oxides obtained in this study possessed somewhat disordered (wormhole-like) pore structures, probably because of low humidity conditions during synthesis (<20% RH), which resulted in rapid H₂O evaporation and limited control over disorder-to-order transition.¹³ Higher BET surface areas were obtained at longer aging times (Table 1) suggesting enhanced condensation and cross-linking in the inorganic framework which led to smaller BJH pore sizes and higher surface areas.

The Tammann temperature (TT) of the metal oxide is another important parameter indicative of the expected thermal stability of mesoporous metal oxides, since the lattice mobility becomes appreciable above TT.¹⁴ V₂O₅, Sb₂O₃, and MoO₃ have relatively low TT (199, 55, and 261 °C, respectively), which may be responsible for the limited thermal stability of corresponding mesoporous oxides. However, Nb₂O₅ possesses a higher TT (619 °C) and is promising as a major component in mixed metal oxides to stabilize their mesoporous frameworks. As shown below, the mesoporous structures of mixed Nb–M oxides were preserved after calcination at 400 °C (Figures 1–3 and Table 1).

Structural Characterization. Further structural characterization was conducted for the best mesoporous phases, which displayed the high surface areas and uniform pore size distributions (Table 1). The SAXS pattern of a representative mesoporous niobium-vanadium oxide (Nb-V-O) calcined at 400 °C is shown in Figure 1. One primary diffraction peak was present at d = 105 Å which was tentatively assigned to a 2D hexagonal structure with the unit cell parameter $a_0 = 121$ Å. This suggested that the thermally stable mesoporous mixed Nb-V-O phase was successfully obtained. The absence of higher order reflections of the 2D hexagonal phase in the SAXS pattern indicated these mesoporous phases lacked the long-range order and suggested the presence of wormhole-like pore structure.



Figure 1. SAXS pattern of mesoporous $V_{0.076}Nb_{0.245}O_x$ phase after calcination at 400 °C (inset: high angle XRD pattern).



Figure 2. TEM image of the mesoporous $V_{0.076}Nb_{0.245}O_x$ phase after calcination at 400 °C.



Figure 3. N_2 adsorption–desorption isotherms and BJH pore size distribution (inset) of the $V_{0.076}Nb_{0.245}O_x$ phase after calcination at 400 °C. The pore size distribution was derived from the N_2 adsorption branch.

Furthermore, the absence of high 2θ angle reflections in the XRD pattern of the calcined Nb–V oxide (Figure 1 inset) indicated the amorphous nature of the inorganic walls in this mesoporous oxide. The TEM image of the calcined Nb–V–O sample (Figure 2) showed a highly porous material possessing disordered wormholelike pores which was consistent with the absence of higher order reflections in the SAXS pattern. It also indicated the presence of ~4 nm thick walls and ~9 nm pores in agreement with the results of the N₂ porosimetry and SAXS (Table 1 and Figures 1 and 3). Similar results were obtained in the case of mesoporous Nb–Mo and Nb–Sb oxide phases.

The N₂ adsorption-desorption isotherms of a representative mesoporous Nb–V oxide are shown in Figure 3. A large hysteresis loop resembling that in a typical H₁-type isotherm was observed for the mesoporous Nb–V–O sample, which



Figure 4. Raman spectra of mesoporous Nb–M–O phases: $V_{0.041}$ -Nb_{0.073}O_x calcined at (A) 600 and (B) 400 °C, (C) Mo_{0.031}Nb_{0.307}O_x calcined at 400 °C, and (D) Sb_{0.54}Nb_{1.52}O_x calcined at 400 °C.

possessed a surface area of 159 m²/g and a pore volume of 0.33 cm³/g. The BJH analysis indicated that the calcined mesoporous Nb–V–O sample exhibited a pore size of 90 Å (Figure 3 inset). The BJH pore sizes, pore volumes and BET surface areas are shown in Table 1 together with theoretical estimates of the surface areas. Theoretical surface areas (S_{Theory}) were estimated as $S_{\text{Theory}} = 4V/D$, which assumes the presence of uniform cylindrical pores with the BJH pore volume V and pore diameter D. The experimental BET surface areas were higher than the theoretical estimates suggesting the presence of structural microporosity consistent with earlier observations of structurally similar mesoporous SBA-15 silicas.¹⁵ In the case of SBA-15 silica, the EO chains of the template partially penetrated the inorganic walls and created microporosity within the inorganic walls after surfaceant removal.¹⁵

The oxides of Mo, V, Nb, and Sb are very important catalytic components for propane (amm)oxidation reactions.⁴ It is wellknown that the surface vanadia and molybdena species are the redox active sites for propane ODH to propylene.¹⁶ The state and dispersion of vanadia and molybdena can dramatically influence the catalytic performance of the VO_r and MoO_r containing catalysts. Therefore, it is important to establish whether vanadia and molybdena were present as molecularly dispersed metal oxide components or separate bulk V₂O₅ and MoO₃ phases. The Raman spectroscopy is a highly sensitive technique for detecting the characteristic vibrations of the metal oxide species and thus can provide direct information about their molecular structures. The isolated VO_x species containing terminal V=O bonds, polymeric VO_x containing bridging V-O-V bonds and the bulk V2O5 phase possess characteristic Raman features that enable their detection in both the bulk and surface-supported vanadia catalysts. The Raman spectra of the hydrated mesoporous Nb-M-O phases after surfactant removal are shown in Figure 4. The reference crystalline niobia (Nb₂O₅) was obtained after the calcination of mesoporous niobium oxide in air at 400 °C for 2 h and then at 600 °C for 3 h. Nb₂O₅ was confirmed by XRD to be the hexagonal phase (JCPDS no. 07-0061). This reference Nb_2O_5 phase showed the characteristic Raman bands at 76, 135, 238, 325, 701, and 832 cm^{-1} (not shown here).

It is well-known that at low metal oxide loadings corresponding to submonolayer surface coverage, only the Raman signals

TABLE 2: Raman Band Assignment	in	Hydra	ted
Mesoporous Nb-V-O and Nb-Mo-	-0	Phases	and
Reference Metal Oxide Species			

san	nple	band (cm ⁻¹)			
Nb ₂ O ₅		701,	325		
V_2O_5		994,	703, 532, 490, 408		
Nb-Mo-C	0-1−400 °C ^a	966, 675			
Nb-V-O-2	2'-400 °C ^a	1035	, 951, 688		
Nb-V-O-2	2'-600 °C ^a	1011, 972, 900, 700, 607			
supported catalyst	dehydrated (cm	l ⁻¹)	hydrated (cm ⁻¹) ²³		
Mo ₃ O/Nb ₂ O ₅	980-1006, ~860-	-910 ²¹	960, 842, 694		
V ₂ O ₅ /Nb ₂ O ₅	1032, ~960 ^{17,18}		$(Ta_2O_5 \text{ as support})$ 994, 940 $(Ta_2O_5 \text{ as support})$		
metal oxide	e species ²³	aqueous solution (cm ⁻¹)			
Mo ₈ O ₂₆	4-	965(s), 925, 590			
$V_{10}O_{28}^{6}$	5—	994(s), 970, 840, 600, 547			
Nb ₂ O ₅ •	nH ₂ O	880, 630			

^a Phases calcined at 400 or 600 °C.

of the 2D surface metal oxide species are present. The Raman bands corresponding to the metal oxide microcrystals usually appear above monolayer surface coverage manifested in a ~994 cm⁻¹ band as well as many other sharp bands in the 200–700 cm⁻¹ range for V₂O₅,¹⁷ and ~820 cm⁻¹ and a weaker band at ~997 cm⁻¹ for MoO₃.¹⁷ The monolayer coverages of polyvanadate¹⁸ and polymolybdate¹⁹ species on Nb₂O₅ were reported to be ~14 μ mol V⁵⁺/m² ²⁰ and ~8 μ mol Mo⁶⁺/m².²¹ Furthermore, the Raman scattering from the metal oxide microcrystals is ~10–100 times stronger than from the corresponding 2D surface metal oxide species.²²

After calcination at 400 °C the mesoporous Nb–V–O (V_{0.041}-Nb_{0.073}O) sample exhibited a Raman band at 1035 cm⁻¹ characteristic of the terminal V=O bonds of dispersed tetrahedral VO_x species, and a broad band near 951 cm⁻¹ that corresponded to the stretching mode of the V–O–V bonds. The 1035 cm⁻¹ band shifted to 1011 cm⁻¹ when the Nb–V–O sample was calcined at 600 °C. The hydrated Nb–V–O sample possessed a Raman band at 972 cm⁻¹ suggesting the presence of the surface V₁₀O₂₈^{6–} species.²³ The bulk Nb₂O₅ was detected in the Nb–V–O phase after calcination at 600 °C by a broad Raman band at 900 cm^{-1.24} No microcrystalline V₂O₅ or MoO₃ was observed in the Raman spectra of the Nb–V–O and Nb–Mo–O phases below 500 °C. In the case of the Nb–Mo–O phase (Figure 4), the band at 966 cm⁻¹ was assigned to the stretching mode of Mo=O, while no microcrystalline Sb₂O₃ was

observed in the case of the mesoporous Nb–Sb–O phase (Figure 4). The absence of microcrystalline oxides of V, Mo, and Sb is not surprising since the total content of these oxides was below or close to their surface monolayer coverage (Table 3). The Raman bands observed for the hydrated mesoporous Nb–V–O and Nb–Mo–O phases are summarized in Table 2, which correspond to the Raman bands typically observed for these surface metal oxide species on various oxide supports or in aqueous solution.²³

Propane ODH. The propane ODH study was carried out for the best mesoporous phases, which possessed the high surface areas and uniform pore size distributions (Table 1). The catalysts used in the propane ODH study were calcined at 400 °C. The reactivity of representative Nb-M-O (M = V and Mo) phases in propane ODH at 425 °C is summarized in Table 3. The main reaction products were CO_x, propylene and water. No appreciable propane ODH activity was observed for the Nb-Sb–O phases, indicating that the surface SbO_x sites were unable to activate propane under experimental conditions investigated. These observations are similar to those made recently by Bañares et al.²⁴ They conducted a propane ammoxidation study of a monolayer supported Sb₂O₃/Nb₂O₅ catalyst at 500 °C, which showed that this catalyst was inactive at this temperature. The low redox activity of the surface SbO_x sites is further supported by the results of a temperature-programmed surface reaction (TPSR) study of a methanol probe molecule conducted by Wachs et al.²⁵ They studied methanol chemisorption and decomposition over a number of redox, acidic, and basic bulk metal oxides and observed that methanol chemisorbed at Sb₂O₃ was oxidized at a significantly higher temperature than that chemisorbed at V_2O_5 and MoO_3 . The ODH reaction rates expressed as the number of μ mol of propane converted per unit surface area per unit time are shown in Table 3. The surface coverages of the VO_x , MoO_x , and SbO_x species in the mesoporous mixed metal oxides of this study were estimated assuming that these oxides were present entirely as the surface species. Furthermore, we employed the experimental VO_x , MoO_x, and SbO_x monolayer surface coverages on the Nb₂O₅ support corresponding, respectively, to 14^{20} , 8^{21} , and 11^{24} µmol/ m². Therefore, for the $V_{0.076}Nb_{0.245}O_x$ phase possessing the BET surface area of 159 m^2/g , the surface vanadia concentration was estimated to be $\sim 12 \text{ V}^{+5} \,\mu \text{mol/m}^2$ corresponding to $\sim 86\%$ of the monolayer VO_x coverage. In the analysis of the observed propane oxidation rates over mesoporous Nb-V oxides, we further assumed that the mesoporous Nb-V-O phases and supported VO_x/Nb₂O₅ catalysts displayed similar intrinsic propane oxidation rates per surface VO_x site. Under these

TABLE 3: Propane ODH over Mesoporous Nb-M (M = V, Mo, and Sb) Oxides and Previously Reported Bulk Dense and Supported VO_x/Nb_2O_5 and MoO_x/Nb_2O_5 Catalysts

Nb-M $-$ O phase $(M = V, Mo, or Sb)$	$S_{\rm BET}$ (m ² /g)	M concn (mol %)	surface M coverage (µmol/m ²) ^d	surface coverage (fraction of monolayer) ^e	propane conversion (%)	selectivity to propylene (%)	rate (µmol/m²s) ^f	refs
2V2O5/Nb2O5a	48	2.0	3.2	0.23	8		0.180	26
$4V_2O_5/Nb_2O_5^a$	46	4.0	6.6	0.47			0.360	26
2% V ₂ O ₅ /Nb ₂ O ₅ ^b	6.8	13.9^{h}	32	2.31			0.167	26
$V_{0.041}Nb_{0.073}O_x$	197	36.0	15.5	1.11	6	72	0.164	this study
$V_{0.076}$ Nb _{0.245} O _x	159	23.7	12.1	0.86	12	46	0.355	this study
MoO _x /Nb ₂ O ₅ ^a	12	5.1^{c}	31.5	3.94	5	62	0.189^{g}	27
$Mo_{0.031}Nb_{0.307}O_x$	159	9.2	4.3	0.54	9	56	0.266	this study
$Sb_{0.54}Nb_{1.52}O_{r}$	197	26.2	9.8	0.88	0	0		this study

^{*a*} Supported catalyst. ^{*b*} Bulk catalyst, 2 wt % V₂O₅/Nb₂O₅. ^{*c*} Corresponds to 5.44 wt % molybdena content of the supported catalyst.²⁷ ^{*d*} Surface coverage calculated assuming that all M is at the surface. ^{*e*} Monolayer coverage of M: 14 V⁵⁺ μ mol/m², 8 Mo μ mol/m², and 11 Sb³⁺ μ mol/m². ^{*f*} Rate of propane consumption per unit surface area. ^{*g*} Calculated as in footnote *f* using the experimental data previously reported.²⁷ ^{*h*} Surface V concentration determined by XPS.

assumptions, the propane oxidation rate over the mesoporous $V_{0.076}Nb_{0.245}O_x$ catalyst was close to that of the supported " $4V_2O_5/Nb_2O_5$ " catalyst²⁶ (Table 3) in which the surface VO_x species was present at $\sim 47\%$ monolayer coverage. These findings suggested that vanadia may be present in the mesoporous Nb-V oxides as both the surface and "bulk" species forming a solid solution with NbO_x in the inorganic walls of the mesoporous phases. Similar conclusions were also reached in the case of the $V_{0.041}Nb_{0.073}O_x$ catalyst (Table 3). Similar assumptions in the case of the $Mo_{0.031}Nb_{0.307}O_x$ phase possessing the BET surface area of 159 m²/g led to an estimated 54% monolayer MoO_x coverage based on the experimental monolayer coverage of 4.6 MoO_x/nm^{2.21} Moreover, this mesoporous $Mo_{0.031}Nb_{0.307}O_x$ phase containing only the 2D surface MoO_x species was more active in propane ODH than the supported MoO_x/Nb_2O_5 catalyst²⁷ (Table 3), in which molybdena was present as both the surface MoO_x species and MoO_3 microcrystals at \sim 4 times the MoO_x monolayer coverage. The BET surface areas, pore size distributions and structural order of these mesoporous mixed metal oxides were not affected by the propane ODH reaction, which was confirmed by the N_2 porosimetry and wide-angle XRD data (not shown here).

Conclusions

Novel thermally stable mesoporous mixed metal Nb-M (M = V, Mo and Sb) oxides were synthesized in the presence of nonionic Pluronic P123 surfactant. The synthesis parameters had a significant impact on the pore structures and chemical compositions of these mixed metal oxides. These mesoporous mixed metal oxides displayed wormhole-like pore structures, high surface areas (up to 200 m²/g), large pore sizes (5-14)nm), and high pore volumes (up to $0.46 \text{ cm}^3/\text{g}$). The Raman spectroscopy demonstrated that the M oxide components (M = V, Mo and Sb) were present as the molecularly dispersed species in mesoporous oxides thermally treated at temperatures as high as 400 °C. The comparison of the propane ODH activity of these mesoporous oxides with that of the model supported metal oxides suggested that the molecularly dispersed VO_x species were present as the 2D surface oxide as well as formed a solid solution with NbO_x in the inorganic walls of the mesoporous phases. The Nb-Mo-O phase containing only the molecularly dispersed MoO_x species displayed higher propane ODH activity than the supported MoO_x/Nb₂O₅ catalyst in which molybdena was present as both the surface MoO_x species and MoO₃ microcrystals. This study further indicated that evaporation-induced self-assembly (EISA) in the presence of nonionic surfactants represents a highly promising method for the

synthesis of thermally stable mesoporous mixed metal Nb–M (M = V, Mo, and Sb) oxides displaying promising pore structures and chemical compositions for selective oxidative functionalization of propane.

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