

Mesoporous Nanocrystalline Mixed Metal Oxides from Heterometallic Alkoxide Precursors: Cobalt–Nickel Oxide Spinel for Propane Oxidation

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Uniform nanocrystalline mesoporous mixed cobalt–nickel spinel phases displaying unimodal pores in the 7–12 nm range and relatively high specific surface areas up to 83 m²/g were prepared by a novel low temperature synthesis approach in which the desired metal oxide stoichiometries were introduced on a molecular level by reacting heterometallic alkoxide precursors in the presence of supramolecular liquid

crystalline phases. The resultant phases, composed mainly of ca. 8–11 nm uniform cobalt–nickel spinel nanoparticles, were highly promising as low-temperature hydrocarbon combustion catalysts investigated in a model reaction of propane oxidation.

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Introduction

Since the discovery of periodic mesoporous silicas^[1] there has been a great interest in developing new materials with diverse compositions, properties and functionalities.^[2] In particular, cobalt and nickel oxides are important materials for current technologies. These materials find applications as heterogeneous catalysts, sensors, electrochromic, electrical and optoelectronic devices.^[3] Cobalt-based catalysts are of great interest in the field of heterogeneous catalysis. In the oxidized state they are active catalysts for the total combustion of organic molecules.^[4] In combination with Mo or W dispersed on an alumina support, they are precursors of sulfided catalysts for hydrosulfurization,^[5] and after pre-reduction, they are highly efficient Fischer–Tropsch synthesis catalysts.^[6] The Co–Fe–O system has been used as a catalyst for low-temperature oxidation of phenol into non-toxic compounds,^[7] while NiO was investigated as a catalyst for the oxidation of CO.^[8] It is well documented that spinels containing transition-metal ions function as efficient catalysts in a number of heterogeneous processes, such as CO oxidation,^[9] catalytic combustion of hydrocarbons^[10] and selective oxidation and reduction of organic molecules.^[11]

In particular, Co- and Ni-based mixed oxides including spinels are frequently used as highly efficient hydrocarbon combustion and partial oxidation catalysts.^[12]

In the past, cobalt–nickel oxide spinels have been prepared by diverse synthetic routes, such as co-precipitation,^[13a,13b] sol-gel^[13c,13d] carbonate decomposition,^[13e] cryochemical,^[13b] spray-pyrolysis.^[13b,13e] However, these synthesis approaches have shown poor control over composition and crystal-size homogeneity. Chi et al.^[13a] prepared hexagonal NiCo₂O₄ spinels (ca. 200 nm) by a co-precipitation method. Although the particle sizes became uniform at calcination temperatures above 400 °C, NiO was present as secondary phase. Lapham and Tseung^[13b] reported the synthesis of NiCo₂O₄ spinels by several synthesis methods, including co-precipitation, salts decomposition, cryochemical and spray-pyrolysis. Although spinel crystal sizes in the order of 5–16 nm were obtained, these phases were composed of non-homogeneous particles with poorly crystalline structures. Furthermore, the presence of undesirable phases such as NiO, Co₃O₄ and NiCoO₂ confirmed metal oxide segregation. Attempts to synthesize NiCo₂O₄ spinels employing sol-gel chemistry have led to poorly crystalline phases with the presence of undesirable NiO, Co₃O₄.^[13c,13d]

Herein, we present the novel soft chemical synthesis of mesoporous nanocrystalline cobalt–nickel spinel by the self-assembly of heterometallic alkoxides in the presence of supramolecular liquid crystalline phases. The use of heterometallic alkoxide precursors allows one to incorporate the desired metal oxide stoichiometries. This novel soft-chemistry approach affords desired bulk compositions in nanocrystalline mixed metal oxides under mild conditions, which prevents metal oxide segregation and eliminates the need for high synthesis temperatures commonly required for so-

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lid-state reactions. The resultant mesophases were investigated in the model reaction of propane oxidation.

Results and Discussion

Several promising synthesis strategies to overcome the limited thermal stability of mesostructured mixed transition-metal oxides have been recently reviewed.^[14] One of these strategies was adopted in this work, i.e. the elimination of strong electrostatic interactions at the inorganic–organic interface by directing the synthesis by weak hydrogen-bonding interactions, and consequently improving the thermal stability of the final mesostructure.^[14a] This was accomplished by using the non-ionic oligomeric surfactant Brij-35 as a structure-directing agent. As inorganic source, an heterometallic single-source precursor ($\text{Ni}_{0.33}\text{Co}_{0.67}$)-(OMe)(acac)(MeOH) was used for the synthesis of mesoporous nanocrystalline cobalt–nickel oxide spinels. 1-Butanol was chosen as a solvent due to its relatively hydrophobic nature, which promotes an enhanced phase separation between the template and the inorganic phase leading to a better defined mesostructure with robust inorganic walls.^[15]

The mesoscopic order of the as-synthesized mixed oxide mesophase was confirmed by SAXS. The SAXS pattern of

the as-synthesized mesoporous Co–Ni oxide phases (Figure 1) showed a single broad peak at a d spacing of ca. 13.5 nm suggesting the formation of a wormhole mesostructure. Upon calcination at 350, 400 and 450 °C, the low 2θ angle peak disappeared and the amorphous walls of the as-synthesized mesophase began to crystallize. In spite of the low 2θ angle peak disappearance for the calcined samples, highly porous mesostructures were observed as confirmed by porosimetry studies. The nitrogen adsorption–desorption isotherms and BJH pore-size distributions on the basis of the adsorption branches of the N_2 isotherms for mesoporous Co–Ni oxide phases calcined at different temperatures are shown in Figure 2. The sample calcined at 350 °C showed a type IV isotherm representative of mesoporous solids with an H2 hysteresis loop, suggesting the presence of ink-bottle-shaped or cage-type pores.^[16] It had a specific surface area of ca. 83 m^2/g with average unimodal pore diameter of 7 nm. The sample calcined at 400 °C also showed a type IV isotherm with an H2 hysteresis loop. It possessed a specific surface area of ca. 35 m^2/g with average unimodal pore diameter of 11.5 nm. Higher calcination temperature led to the collapse of the mesoporous structure as shown in part c of Figure 2. This sample calcined at 450 °C shows only a specific surface area of ca. 12 m^2/g with disordered random pore-size distribution, indicating the formation of a nonmesoporous structure. The moderate alkaline conditions employed in our synthesis near the isoelectric point of both hydroxo systems, i.e. pH ca. 8 for Co^{3+} and pH ca. 8–10 for Ni^{2+} ,^[17] enhanced the condensation of the Co and Ni ions at the micellar interface. Furthermore, the synthesis conditions near the isoelectric point were favorable for the mesostructural organization of the Co–Ni–O species enabling the formation of heterometallic sol particles. The enhancement in cross-linking of the inorganic framework may be in part responsible for the thermal stability of these mesophases. Furthermore, the TEM image of the thermally stable mesoporous Co–Ni oxide phase shown in Figure 3 confirmed the presence of highly porous nanostructured aggregates. An average pore diameter of ca. 7–8 nm can be observed in agreement with the nitrogen porosimetry data.

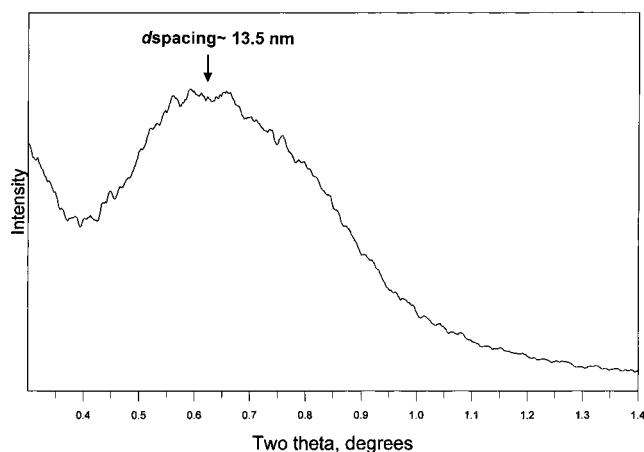


Figure 1. SAXS pattern of the as-synthesized mesoporous Co–Ni oxide phase.

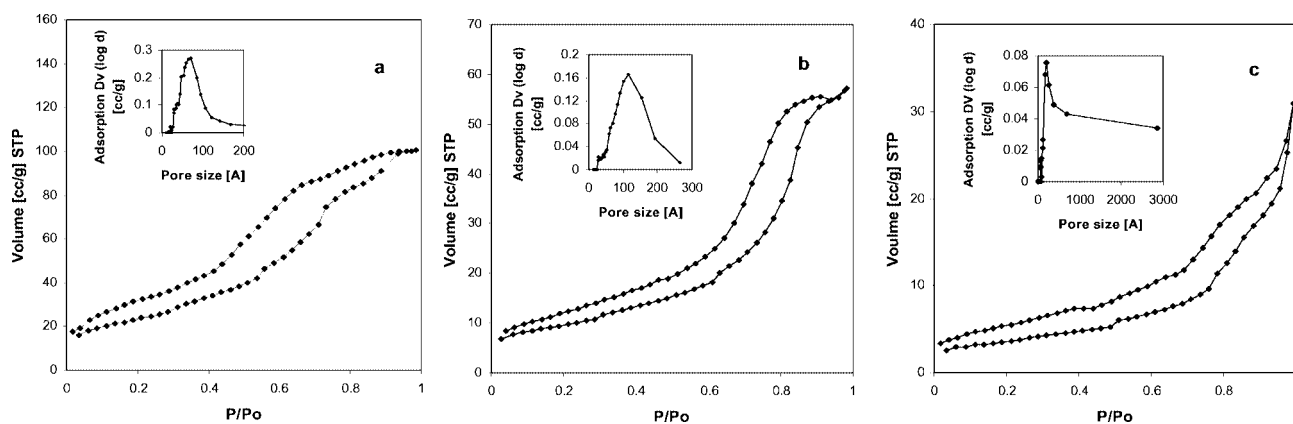


Figure 2. Nitrogen adsorption-desorption isotherms and pore size distribution of mesoporous nanocrystalline cobalt–nickel oxides calcined at (a) 350 °C, (b) 400 °C and (c) 450 °C.

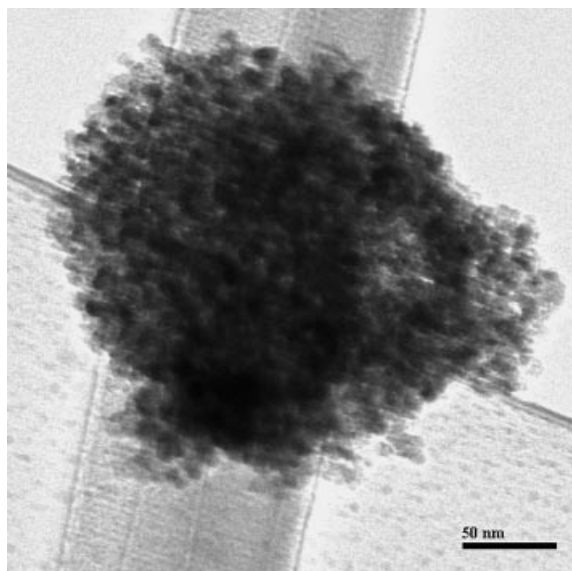


Figure 3. TEM image of mesoporous nanocrystalline cobalt–nickel oxide spinel calcined at 350 °C.

These uniform mesoporous nanostructures were composed of NiCo_2O_4 and NiO nanocrystals. Despite the crystallization of amorphous walls upon calcination, the composition of the spinel phase remained essentially the same as that of the original heterometallic alkoxide precursor. Table 1 summarizes the textural properties and spinel average crystal size of the mesoporous cobalt–nickel oxide phases at different calcination temperatures. Figure 4 shows the PXRD patterns of the cobalt–nickel oxide phases as a function of calcination temperature, whereas Table 2 summarizes their compositional and structural properties. The structural properties of the uniform nanocrystalline mesoporous phases were determined using Topas profile fitting software.^[18] These findings indicated that the spinel content remained practically unchanged at 81–84% for samples cal-

cined at 350 °C and 400 °C, whereas the nanoparticle size increased from 8.4 nm to 11.1 nm, respectively, due to progressive crystal growth. A remarkable change in compositional and structural properties is evident for the sample calcined at 450 °C. This particular sample contained only 73% of 20.6 nm spinel nanocrystals. The excessive crystal growth at higher calcination temperatures was responsible

Table 1. Selected textural properties and spinel average crystal size of mesoporous nanocrystalline cobalt–nickel oxides as a function of calcination temperature.

Sample	Average pore size [nm]	Specific surface area [m^2/g]	NiCo_2O_4 particle size [nm]
mesoporous/350 °C	7.0	83.8	8.4
mesoporous/400 °C	11.5	35.0	11.1
mesoporous/450 °C	–	12.1	20.6

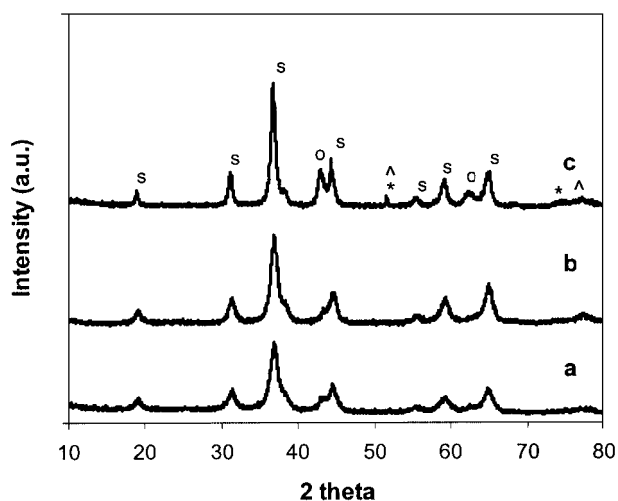


Figure 4. PXRD patterns of mesoporous nanocrystalline cobalt–nickel oxides calcined at (a) 350 °C, (b) 400 °C and (c) 450 °C. s = NiCo_2O_4 , o = NiO , * = Ni , ^ = Co .

Table 2. Compositional and structural parameters of mesoporous nanocrystalline cobalt–nickel oxides as a function of calcination temperature.

T [°C]	Phase	Phase content [wt.-%]	Lattice parameter [Å]	Volume [Å ³]	Mean domain size [nm]	Lattice disorder, e_0 ^[a]
350	NiCo_2O_4	81.1	8.14	539	8.4	0.22
	<i>Fd3m</i>					
	NiO	17.1	4.19	73.1	9.7	0.70
	<i>Fm3m</i>					
400	Ni,Co	0.80	3.54	44.3	19.4	0.01
	<i>Fm3m</i>					
	NiCo_2O_4	83.8	8.13	538	11.1	0.12
	<i>Fd3m</i>					
450	NiO	15.8	4.19	71.0	14.2	0.95
	<i>Fm3m</i>					
	Ni,Co	0.40	3.54	44.4	19.5	0.00
	<i>Fm3m</i>					
450	NiCo_2O_4	73.2	8.13	537	20.6	0.19
	<i>Fd3m</i>					
	NiO	25.8	4.21	74.4	18.8	0.43
	<i>Fm3m</i>					
450	Ni,Co	1.0	3.54	44.4	20.5	0.00
	<i>Fm3m</i>					

[a] The lattice disorder (measured as an average strain, e_0) is directly related to the atomic disorder of the metals in the lattice.

Table 3. Catalytic properties of dense Co–Ni–O spinel and mesoporous Co–Ni–O oxides in propane combustion at 280 °C. Feed: 6.3 vol.-% propane, 9.4 vol.-% O₂ and balance He.

Catalyst	C ₃ conversion mol-%	S(CO) ^[a] mol-%	S(CO ₂) mol-%	C ₃ combustion rate nanomol/m ² s
dense spinel	11	79	21	1.76
mesoporous/350 °C	59	37	63	1.40
mesoporous/400 °C	64	31	69	3.59
mesoporous/450 °C	9	29	71	1.42

[a] *S* = selectivity.

for the mesostructure collapse. Traces of Ni and Co metals were also detected in all three mesoporous samples.

The morphological changes of the uniform mesoporous mixed Co–Ni oxide phases as a function of calcination temperature are shown in Figure 5. The sample calcined at 350 °C was very uniform containing spheroidal ca. 8.4-nm spinel nanoparticles. The sample calcined at 400 °C contained spheroidal ca. 11.1-nm spinel nanoparticles as well as rhombohedral crystals of some minority phase, probably NiO. Excessive growth of spinel nanocrystals within the channel walls of the inorganic framework led to the formation of well-defined hexagonal and rhombohedral 20-nm spinel nanocrystals which disrupted the mesoporous structure.

The CH analysis (Robertson Microlit Laboratories) indicated that only 0.42, 0.66 and 0.30% C remained in the 350, 400 and 450 °C calcined mesoporous Co–Ni oxide phases, respectively.

Table 3 shows representative catalytic properties of the uniform mesoporous Co–Ni oxides and a dense Co–Ni oxide spinel in propane combustion. The mesoporous catalysts calcined at 350 and 400 °C were much more active in propane combustion than the dense spinel and mesoporous catalyst calcined at 450 °C. These catalysts showed a high degree of propane conversion to CO and CO₂ at the same gas space velocity indicating that these mesoporous Co–Ni oxides contained a higher number of active surface sites, whereas the catalytic behavior of the mesoporous Co–Ni oxide calcined at 450 °C was similar to that of the dense spinel, confirming that the former phase was no longer mesoporous. The catalytic data were further analyzed in terms of propane combustion rate normalized by the surface areas of these model catalysts. Some variation of the propane combustion rate was observed (Table 3) suggesting that the nature of the active surface sites was largely unaffected by the self-assembly process. Moreover, the mesoporous catalysts calcined at 350 and 400 °C were significantly more selective to CO₂ than CO as compared to the dense spinel phase, which is highly desirable for catalytic combustion applications. We believe that the mesoporous samples showed superior catalytic behavior not only due to their greater surface areas and mesoporous structure, but also because of the relatively small size of the spinel crystallites. In particular, the higher combustion rate observed for the mesoporous sample calcined at 400 °C suggests the existence of optimal crystallite size in the nanoscale regime. Furthermore, the presence of mesoporous channels en-

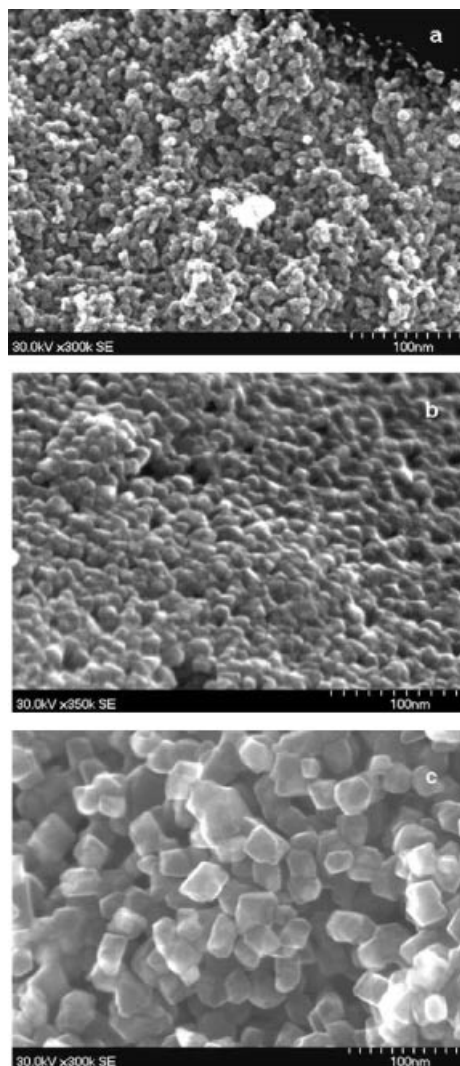


Figure 5. High resolution SEM images of mesoporous nanocrystalline cobalt–nickel oxides calcined at (a) 350 °C, (b) 400 °C and (c) 450 °C.

hanced the diffusion of reactant and product molecules and improved the mass-transfer characteristics of Co–Ni–O spinels.

Conclusions

Uniform nanocrystalline mesoporous cobalt–nickel oxide spinels were prepared by employing a heterometallic

alkoxide precursor and oligomeric alkyl-ethylene oxide surfactant as a structure-directing agent. These resultant mesoporous phases displayed unimodal pores in the 7–12 nm range and relatively high specific surface areas up to 83 m²/g. The mesoporous phases were composed mainly of ca. 8–11 nm Co–Ni–O spinel nanocrystals. These nanocrystalline uniform cobalt–nickel oxides were studied as catalysts in the combustion of propane, showing higher propane conversion to CO and CO₂ as compared to a conventional dense spinel. This improved catalytic behavior may be related to their morphological and structural advantages such as larger surface area and mesoporous structure, and to the relatively small size of the spinel crystallites. Furthermore, this soft chemistry method is highly promising for the general synthesis of nanocrystalline and mesoporous mixed metal oxides with desired bulk stoichiometries from heterometallic alkoxide precursors in the presence of supramolecular liquid crystalline phases.

Experimental Section

Synthesis of the Heterometallic Single-Source Alkoxide Precursor:

The heterometallic single-source precursor (Ni_{0.33}Co_{0.67})(OMe)-(acac)(MeOH) was obtained as follows. Na (2.517 g, 109 mmol) was refluxed in a solution of anhydrous toluene (50 mL), 2-methoxyethanol (12.5 mL, 164 mmol) and acetylacetone (5.5 mL). A mixture anhydrous CoCl₂ (4.934 g, 36.5 mmol) and Ni(NH₃)₆Cl₂ (4.209 g, 18.2 mol) was added to the above solution under vigorous stirring. The resultant heterogeneous mixture was refluxed for 2 h, diluted with additional 20 mL of toluene and refluxed again for another 2 h. The voluminous sediment of NaCl was precipitated overnight and the purple solution transferred into a separate flask and the solvents evaporated to dryness leaving a viscous purple liquid. It was dissolved then in 50 mL of anhydrous MeOH. The formation of purple red prismatic crystals started almost immediately. The mixture was left overnight in a freezer at –30 °C and the solid product was then separated by decantation, washed with 5 mL of cold MeOH and dried *in vacuo*. The purity of the resultant heterometallic Co–Ni alkoxide was confirmed by elemental analysis and IR. Yield: 9.124 g (76%). (Ni_{0.33}Co_{0.67})(OMe)(acac)(MeOH) (221.04): calcd. C 38.0, H 6.4; found C 37.6, H 6.3. IR: $\tilde{\nu}$ = 3221 (s br), 1603 (vs br), 1515 (s), 1397 (s), 1255 (m), 1193 (w), 1124 (w), 1045 (s), 1033 (sh), 1014 (m), 922 (m), 765 (m), 636 (w), 571 (m), 554 (m), 435 (s), 416 (s) cm^{–1}. This heterometallic Co–Ni alkoxide was used as inorganic precursor.

Synthesis of Mesoporous Nanocrystalline Cobalt–Nickel Oxide Spinel:

The mesoporous nanocrystalline cobalt–nickel oxide spinels were prepared as follows. The synthesized heterometallic single-source alkoxide precursor (see above) was dissolved in 1-butanol (Aldrich, 99.9%) and heated at 70 °C. Separately, the oligomeric alkyl-ethylene oxide surfactant Brij-35 [C₁₂H₂₅(OCH₂CH₂)₂₃OH, Aldrich] was dissolved in butanol and then added to the inorganic precursor solution. This solution was stirred at room temperature for 3 h, and then precipitated with NH₄OH 1 M (Fisher Chemicals) at pH = 8.0–9.0. The resultant grayish slurry was aged in an open Petri dish at 50 °C for 2 d, and then dried at 90 °C for 1 d to yield brownish powders upon evaporation. The as-synthesized powders were calcined at 350 °C, 400 °C and 450 °C to remove the template and increase crosslinking of the inorganic framework. Typical synthesis compositions on weight basis were 1-butanol:surfactant = 21–26; precursor:surfactant = 0.55–0.60; precursor:solvent =

0.023–0.026. The surfactant volume fraction expressed as $V_{\text{template}}/(V_{\text{template}} + V_{\text{inorganic}})$ was kept constant at $\phi = 0.20$ –0.25. A reference sample of dense Co–Ni oxide spinel was also prepared as described above, but without the addition of the structure directing agent. This dense phase was calcined at 450 °C.

Characterization: The nitrogen adsorption–desorption isotherms were measured with a TRI-STAR 3000 porosimeter. The pore-size distributions were calculated from the adsorption branch of the isotherm using the BJH method. The PXRD was measured with a Siemens D5000 diffractometer using high power Ni-filtered Cu- K_{α} radiation with $\lambda = 1.54178$ Å source operating at 50 kV/35 mA. High-resolution SEM analysis was performed with Hitachi S-5200 (30 kV, 10 mA). The samples for SEM were deposited onto carbon film-supported 200 mesh copper grids. The SAXS pattern was collected in a Hi-Star area two-dimensional multiwire proportional counter detector (BRUKER AXS GADDS system, $\lambda = 1.5418$ Å). The TEM image was captured with a GATAN multi-scan digital camera mounted on a JEOL 2010F. The TEM sample was prepared by depositing a small amount of powder on a lacey carbon 200 mesh copper TEM grid. Propane oxidation was conducted at 350–450 °C using a feed of 6.3 vol.-% propane, 9.4 vol.-% oxygen and balance He and ca. 0.1 g of catalyst packed in a 3/8"-quartz tubular microreactor in a programmable oven. The flow rate was 4.2 cm³/min in all cases. An HP 5890II gas chromatograph equipped with an FID and TCD was employed for the reaction product analysis. The carbon balances agreed within 5 mol%.

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