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# Pore structure effects on the kinetics of methanol oxidation over nanocast mesoporous perovskites

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## ABSTRACT

Mesoporous LaMnO<sub>3</sub> perovskite catalysts with high surface area were synthesized by using the recently developed hard templating method designated as “nanocasting”. Ordered mesoporous silica designated as SBA-15 was used as the hard template. It was found that the surface area of the nanocast perovskites can be tuned (80–190 m<sup>2</sup>/g) by varying the aging temperature of the SBA-15 template. Nanocast LaMnO<sub>3</sub> catalysts showed high conversion efficiencies for the total oxidation of methanol under steady state conditions, the one with the highest value of surface area being the best catalysts, as expected. Kinetic studies were performed for all of the synthesized catalysts. Rate constants were found to vary in accordance with the specific surface area of the nanocast catalyst which depends on the aging temperature of the parent template. From the rate constants obtained from experimental conversions at various space velocities (19500 to 78200 h<sup>-1</sup>), values of activation energy and pre-exponential factor for the three nanocast LaMnO<sub>3</sub> catalysts were determined by the linear regression of the Arrhenius plot. It is observed that the activation energy for all the catalysts remain constant irrespective of the variation in specific surface area. Further, a linear relationship was found to exist between the pre-exponential factor and specific surface areas of the catalysts indicating that the rates per unit surface area remains the same for all the catalysts.

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## 1. Introduction

Development of strategies in order to limit the emission of toxic gases such as volatile organic compounds (VOC) from industrial processes is one of the major challenges of the present time. It is desirable to develop environmentally friendly technologies to eliminate pollutants without resulting in further toxic by-products. Thermal combustion is effective; however, using a catalyst can result in much better conversion rate at a comparatively lower temperature by altering the kinetics. For this reason, various scientific efforts were made to develop

novel catalytic materials for that purpose [1,2]. Even though noble metals were found to be effective in most of the reactions concerned, it is not at all a cost effective solution from an industrial perspective. Interestingly, perovskite structured mixed metal oxides (ABO<sub>3</sub>) were found to be as effective as noble metals for various catalytic partial or total oxidation reactions especially those of hydrocarbons and volatile organic compounds [3,4]. However, the applicability of these materials is not yet fully exploited since the high temperature (> 700 °C) conditions used in the synthesis of these materials result in very low specific surface area (< 30 m<sup>2</sup>/g) [4–8]. Hence a major

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milestone that needs to be achieved for the effective utilization of these materials on an industrial scale is the development of a synthesis strategy that helps to achieve higher surface areas. On this regard, Kaliaguine *et al.* [9] successfully synthesized perovskite oxides with higher surface areas (100 m<sup>2</sup>/g) where calcination is performed at temperatures around 200 °C. However, in this case also, the specific surface area was found to decrease at higher calcination temperatures.

The discovery of ordered mesoporous silica and the developments that followed on the research focusing on various mesoporous materials in the past two decades have made it possible to also synthesize various non-siliceous composition materials (carbon, metal oxides, carbides, etc) with extremely high values of specific surface areas [10,11]. Out of the methods available for the synthesis of mesoporous materials, *nanocasting* enjoys a unique position. This method is found to be efficient for developing mono-metallic and/or mixed oxides with high specific surface areas [12–15], which cannot be obtained using other methods. Various studies were performed utilizing the nanocasting approach for the synthesis of a variety of compositions which were successfully utilized for a wide range of applications [16–20, see also literature cited in 15]. Even though these nanocast oxides were examined for a large number of catalytic reactions, most of such studies focused on the measurement of temperature dependent conversions as a function of catalyst composition or surface area [14,21–25]. For the successful employment of these materials in the industry advanced knowledge on the surface reactions as well as the reaction kinetics is required.

We have recently reported the synthesis and catalytic studies of mesoporous perovskite oxides with high specific surface area synthesized using the method of nanocasting [15]. Our studies clearly demonstrated the higher catalytic efficiency of the nanocast perovskites compared to their bulk counterparts synthesized using reactive grinding method and conventional citrate method for various gas phase reactions. To supplement our previous study [15], we report here on the synthesis of high surface area LaMnO<sub>3</sub> materials using SBA-15 silica aged at different temperatures (35, 100 and 140 °C) as the hard templates, and discuss the influence of the porosity parameters of the thus-obtained perovskites on their catalytic activity and kinetics. The catalytic properties of these high surface area materials were studied for the total oxidation of methanol. The surface and redox properties of the materials were analyzed using temperature-programmed characterization methods. Detailed kinetic data processing was performed for these materials to achieve a better understanding of the high catalytic efficiencies observed for these new materials.

## 2. Experimental

### 2.1. Synthesis of ordered mesoporous SBA-15 silica

Ordered mesoporous silica SBA-15 hard templates were synthesized according to the previously reported procedure, using Pluronic P123 as the structure-directing agent and tetraethylorthosilicate (TEOS) as the silicon source [26]. In a typical

synthesis, 4.0 g of P123 was dissolved in 76 g of deionized water and 2.3 g of hydrochloric acid (37%) at 35 °C under magnetic stirring. To the obtained homogeneous solution, 8.6 g of TEOS was rapidly added with continued stirring for 24 h at 35 °C and subsequently subjected to hydrothermal treatment at a desired temperature (35, 100 and 140 °C) for an additional 24 h to ensure further framework condensation. After cooling, the resulting solution was filtered and the solid products were dried at 100 °C for 24 h. Finally, the powders were calcined at 550 °C in order to remove the organic copolymer template.

### 2.2. Nanocasting of mesoporous perovskites

Nanocasting of the mesoporous perovskites was performed by the previously reported procedure using a citrate complex of metal cations as the perovskite precursor and ordered mesoporous silica SBA-15 as the hard template [15]. The precursor was impregnated into the template by using the wet impregnation method. In a typical synthesis, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Mn(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O (3 mmol each) were dissolved in an ethanolic solution of citric acid (10 mL) to obtain an equimolar solution, which was added slowly to SBA-15 (1 g) dispersed in water (10 mL). The molar ratio of total metal ions and citric acid was kept at 2:1. The mixture was stirred for a few hours at room temperature, and then the solvent was evaporated under vacuum with a rotary evaporator. The powder thus obtained was further dried at 80 °C for 24 h, ground well in a mortar, and calcined at 500 °C for 4 h to remove the organic part. Impregnation was repeated twice, using for the second time one half of the amount of the precursor, to achieve higher loadings. The final powder was calcined at 700 °C for 6 h, and the silica template was then removed by treating the composite 3 times with NaOH (2 mol/L) at room temperature. The obtained product was washed with water and ethanol and dried overnight at 80 °C. Three syntheses were performed using template SBA-15 aged at 35, 100 and 140 °C and here after, these samples will be denoted as LaMnO<sub>3</sub>-35, LaMnO<sub>3</sub>-100 and LaMnO<sub>3</sub>-140, where the numbers indicate the aging temperature of the SBA-15 template used.

### 2.3. Characterization

Wide-angle powder XRD was performed with a Siemens Model D5000 diffractometer using Cu K<sub>α</sub> radiation ( $\lambda = 0.15496$  nm). N<sub>2</sub> physisorption analyses were performed at -196 °C with an ASAP 2010 sorption analyzer. Prior to analysis, the samples were degassed overnight at 150 °C. Specific surface areas of nanocast perovskites were calculated using the BET method on the lower relative pressure region of the isotherm (0.05–0.2). Pore size distributions were obtained by using the NLDFT method assuming cylindrical pore geometry (applying the kernel of metastable NLDFT adsorption isotherm, i.e., adsorption branch) supplied by the Autosorb-1 1.55 software from Quantachrome Instruments [27–29]. The total pore volume was calculated from the N<sub>2</sub> sorption capacity at  $p/p_0 = 0.95$ . Elemental analysis was performed using an M1100 B Perkin-Elmer atomic absorption spectrophotometer. For TEM

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