

Nano clusters of Li/MgO as efficient catalyst for oxi-dehydrogenation of propane to olefins

Cristiano Trionfetti¹, Igor V. Babich, K. Seshan* and Leon Lefferts
¹Catalytic Processes and Materials, Faculty of Science and Technology, IMPACT,
University of Twente, Enschede, The Netherlands
*k.seshan@tnw.utwente.nl

Introduction

The current demand for olefins, in particular propylene, makes catalytic oxidative dehydrogenation (ODH) of alkanes to olefins an important option as a conceptually promising alternative to steam cracking and catalytic dehydrogenation. Low olefin yields (< 35%) are the bottleneck in catalyst development; typical red-ox type catalyst systems studied so far cause extensive sequential olefin combustion [1]. In this context, alkali promoted MgO, catalyst with no formal redox properties, is a promising catalytic system for oxidative conversion of LPG; high activity and selectivity towards olefin (yields >50%) is reported [2]. In the case of methane oxidation, Lunsford *et al.* suggested that, for these catalysts, [Li⁺-O⁻] type defect sites are responsible for the catalytic activity [3]. Further, it was suggested that hydrocarbon activation occurred on these sites forming alkyl radicals, followed by reactions in the gas phase to form products [3]. Formation of such defect sites is an activated process and requires high temperature treatment (>750°C). This causes sintering (facilitated also by presence of alkali), loss of surface area, and limits the efficiency of the catalyst. Sol gel method allows preparation of high surface area Li/MgO nanoclusters (particle size less than 20 nm). This helps in the incorporation of Li ions in MgO lattice as defects, even after calcination at temperature as low as 500°C, as well as formation of an appreciable amount of low coordinated [Mg²⁺_{LC} O²⁻_{LC}] sites [4]. Understanding the relationship between type of surface sites and catalytic performance of Li/MgO nanoclusters in propane ODH will be the main objective of this presentation.

Materials and Methods

Nanoscale Li/MgO materials have been prepared by sol-gel method starting from Mg(OCH₃)₂ and LiNO₃ methanol solutions. All steps in the preparation have been followed with FTIR, TG/DTA/MS measurements. The obtained catalysts were characterized using XRD, BET adsorption, TEM and FTIR of adsorbed probe molecules (i.e. CO and H₂) at nitrogen liquid temperature (77 K). Surface oxidation activity at high temperature (500°C) was studied using isotopic oxygen exchange and N₂O as probe molecule. Catalytic tests for propane conversion have been performed in a fixed-bed reactor with GC and MS analysis.

Results and Discussion

Transformations that occur during gel formation i.e. hydrolysis and condensation, are influenced by the presence of LiNO₃. Indeed, when co-gelling Mg(OCH₃)₂ and LiNO₃ it has been found that Li⁺ as well as (NO₃)⁻ ions are capable to terminate alkoxi-chains. Thus Lithium is located as a terminating entity i.e. -Mg-O-Li gives rise to incorporation of lithium in magnesia under mild conditions. Moreover calcinations of the gels result in oxide clusters of about 5-20 nm and therefore high surface area Li/MgO solid solutions can be achieved.

Incorporation of Li⁺ ions in the MgO lattice gives rise to oxygen vacancies (Fig. 1a). These would generate Mg²⁺ sites with lower number of oxygen ions neighbors. By means of FTIR spectroscopy of adsorbed CO, we can show that nanoscale Li/MgO catalysts prepared present low coordinated sites - Mg²⁺_{LC} - cations with coordination numbers 3, 4 or 5 and their relative abundance depends on the lithium concentration. A confirmation of the presence of an enhanced concentration of surface oxygen vacancies due to incorporated lithium comes from (i) isotopic oxygen exchange measurements, as the rate of exchange is dependent on the lithium content and (ii) by N₂O decomposition (related to oxygen vacancies) which increased with increasing Li doping. A competition between O₂ and N₂O molecules for the investigated sites was also recorded at 500°C clearly showing that the sites responsible for N₂O conversion can also activate O₂ gas molecules at relative low temperature. Sol-gel Li/MgO catalysts perform surprisingly well in ODH of propane already at 500°C showing high selectivity to olefins and the rate of propane conversion per m² of catalysts increases with increasing lithium doping. A comparison between sol-gel catalyst and conventionally prepared catalyst (bulk) has been made at low conversion level of propane (up to 6%); at 550°C sol-gel catalyst showed higher activity than bulk catalyst as well as better selectivity to olefins (65 % sol-gel and 55% bulk, fig.1b). The significant higher selectivity to olefins for sol-gel catalysts might be due to the contribution of additional sites, for instance low coordinated [Mg²⁺_{LC} O²⁻_{LC}] sites. Their role in ODH of propane will be discussed.

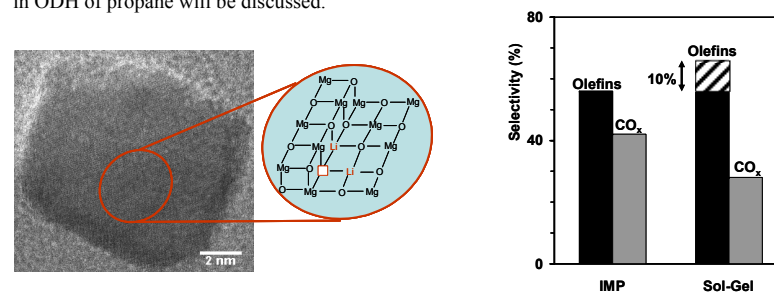


Figure 1. a) TEM picture for nano-particle size of 1 wt% Li/MgO catalyst by sol-gel method; b) Li/MgO by sol gel method and wet impregnation (IMP) tested in ODH of propane at T=550°C; selectivity to olefins was calculated at the same level of propane conversion.

Significance

Nano-structured Li/MgO catalysts with enhanced catalytically active defect sites [Li⁺O⁻] can be synthesized by sol-gel method. These catalysts show improved olefin yields. Role of various defect sites is discussed.

References

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