

How to explain the highest basic reactivity of the weak basic OH sites compared to the strong basic O²⁻ sites of MgO ?

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Introduction

The interest in basic solid catalysts has been recently renewed because of the development of basic catalysts for fine chemistry.[1] MgO is considered as a good model system to investigate how basic sites work at molecular level. However, in a highly divided powdered sample, there are a large range of surface basic sites: i) the oxide ions O²⁻_{LC} (LC= Low coordination) that are revealed by high temperature treatment; it was shown that the lower the coordination number of basic oxide ions, the higher their deprotonation ability (thermodynamic Brønsted basicity) and the higher their basic reactivity in decomposition of 2-methylbut-3-yn-2-ol (MBOH).[2] ii) the hydroxyl groups that cover the surfaces treated in lower temperature range ; despite poorer thermodynamic basicity, hydroxyl groups are much more reactive than oxide ions. The aim of the present work was to rationalize this behaviour thanks to an experimental and theoretical approach.

Materials and Methods

MgO samples were prepared with various morphologies. Hydroxylated surfaces were obtained by rehydration at room temperature of carbonate and OH free samples (obtained by a first treatment at 1073 K). Their OH coverage was varied by a further evacuation at increasing temperature. MBOH isosurface conversion experiments were performed at 393 K. O_{LC}H⁺ were characterized by DRIFTS [2] and ¹H MAS NMR [3]. The hydroxylated forms of the surface defects presented on fig. 1 were modelled by periodic (VASP) [4] and cluster approaches (Gaussian 03) in the framework of Density Functional Theory. The ν_(OH) infra red frequencies [5], proton nuclear shieldings [6] were calculated. The intermediates in MBOH conversion were modelled on hydroxylated and dehydroxylated MgO surfaces.

Results and Discussion

Among the numerous types of O_{LC}H⁺ present on MgO surfaces, only some of those leading to the IR band at 3740 cm⁻¹ are directly involved in basic reactivity. DFT calculations indicate that most of them are hydrogen bonded, and that both IR frequencies and ¹H NMR chemical shifts depend to first order on their hydrogen acceptor and donor character. Finally, a quantitative correlation between ¹H MAS NMR and MBOH conversion evidences that the

active O_{LC}H⁺ are the less coordinated O_{1C}H⁺ and O_{2C}H⁺ formed by hydroxylation of Mg²⁺ cations (fig.2). Their accessibility, flexibility and involvement in H bonding interactions may explain their peculiar reactivity. Several mechanisms can be proposed and their validity is evaluated by computational approach. The adsorption structures of reactants and products are compared on dehydroxylated and hydroxylated surfaces. It is shown that the transformation step of adsorbed MBOH into adsorbed products is less endothermic on hydroxylated surfaces. Work is in progress to determine if it results in a more stabilized transition state that could explain the surprising high reactivity of weak bases.

Significance

A multi-techniques experimental and theoretical approach allows i) to discriminate the numerous surface O_{LC}H⁺ ions of MgO by two complementary spectroscopies, ii) to identify the O_{1C}-H and O_{2C}-H as the most catalytically active hydroxyls thanks to ¹H MAS NMR, iii) to discuss mechanistic aspects, and finally rationalize why despite their poor thermodynamic Brønsted basicity, O_{LC}H⁺ ions are much more reactive than their O²⁻_{LC} analogs in MBOH conversion. This work enlightens promising perspectives for the development of new basic catalysts involving weak basic sites.

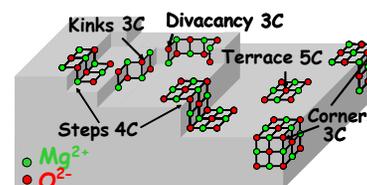


Figure 1: Representation of the various types of O²⁻_{LC} on defective MgO surfaces.

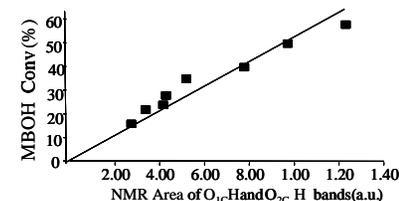


Figure 2: Correlation between MBOH conversion and O_{1C}H⁺ and O_{2C}H⁺ NMR contributions.

References

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