

Nature of hydroxyl groups acting as basic sites on MgO surfaces

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Introduction

On free carbonates MgO surfaces, water dissociation generates $O_{LC}H$ groups (L: coordination number of oxygen), either by protonation of a O_{LC}^{2-} anion (L = 3: corner, 4: edge, 5: face) or from hydroxylation of a Mg^{2+} cation (L = 1 or 2, 3 when O is bridging).[1] In previous studies, the role of OH groups in the basic reactivity of MgO has been evidenced: despite a lower basicity than that of O^{2-} ions, they are more reactive in the conversion of 2-methylbut-3-yn-2-ol (MBOH).[2] **The aim of this work is to identify the nature of the most reactive hydroxyl groups by means of IR and 1H MAS NMR spectroscopies. The assignment of the composite bands is made on the basis of theoretical results and the relation between the state of the surface and the catalytic behavior is investigated.**

Materials and Methods

MgO samples of various morphologies were prepared.[3] Treated at 1023 K, they are highly dehydroxylated and possess different amounts of low coordinated sites (table 1). Hydroxylated surfaces are obtained by subsequent hydration and evacuation at increasing temperature T_i . MBOH isosurface conversion experiments are performed at 393 K, with $P_{MBOH} = 3.3$ kPa and $T_i = 673$ K. OH groups are characterized by DRIFTS and 1H MAS NMR ($B_0 = 9.4$ T, spinning rate: 12.5 kHz). Hydroxylation of defects on MgO surface have been modeled by periodic (VASP) and cluster approaches (Gaussian 03) and the nuclear shielding calculated.

Results and Discussion

Former results have shown by varying T_i for the same sample, that active OH groups vibrate in the IR band located at 3740 cm^{-1} . [2] However, the catalytic conversion of the different materials, treated at the same evacuation temperature T_i , is not correlated to the intensity of this band (table 1). Because calculations show that this band contains different sorts of OH groups (formed on Mg_{LC}^{2+} and on very defective $Mg^{LC}O^{LC}$ pairs), it is concluded that only some of these OH are active.

Table 1. Catalysis and IR results for different hydroxylated samples

Sample	MgO-precipitation	MgO-hydration	MgO-sol-gel
Lowest coordinated sites concentration*	→		
Conversion (%) (for 5 m^2)	57.6	48.9	36.2
IR ν_{OH} band (3740 cm^{-1}) area (per m^2)	0.54	0.90	1.48

* Obtained from photoluminescence spectroscopy analysis [3]

In order to better experimentally discriminate between the different OH groups, 1H MAS NMR has been used. Providing that handling of the pretreated sample and filling of the

rotors is performed in a glove box, well defined spectra were obtained (Figure 1). Moreover, since $O_{1C}H$ and $O_{2C}H$ are not expected from methanol adsorption, comparison of the NMR spectra obtained after hydration or CD_3OH adsorption (Figure 1) was made, showing that $O_{3C}H$ and $O_{4C}H$ exhibit the highest chemical shift.[4]

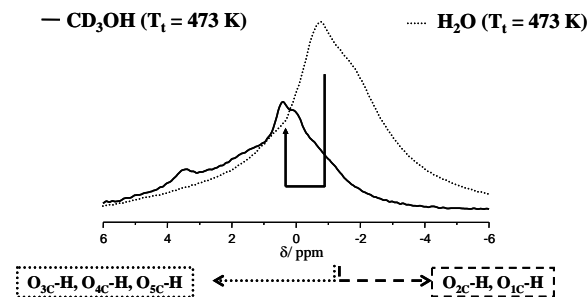


Figure 1. Assignment of 1H NMR spectra of hydroxyls on MgO, by comparison of experiments and calculations.

Calculations confirm these preliminary results and give a precise description of OH groups environment in each chemical shift range. Decomposition of the NMR signal was then made. It is shown that on a series of different samples with different level of hydration, the area of the NMR contribution of the less coordinated OH groups is well correlated with the catalytic activity.

Conclusion

It was then concluded that active sites are $O_{1C}H$ and $O_{2C}H$, located at low chemical shift in 1H MAS NMR. A mechanism has been proposed considering that the active sites are the less coordinated OH groups thus that they can behave as Lewis basic sites.

Significance

This fundamental work shows that low coordinated OH groups can be very reactive species. Thus the role of basic site in a catalytic reaction may be revisited on the basis of these results. This work is also a typical example of mixed experimental-theory approach.

References

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