Alcohol model reaction networks for basicity characterization

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Introduction

The characterization of acido-basic properties of the surface of inorganic solids is essential to understand the behavior of heterogeneous catalysts. The use of alcohols as reactive probe molecules to investigate these properties has been developed since the 1970s, and in 1991, a new alcohol, 2-methylbut-3-yn-2-ol (MBOH), was proposed [1]. The aim of this work is first to sum up the knowledge accumulated over 15 years on this model reaction showing that MBOH appears to be a valuable reactive probe molecule to characterize the basic sites.

The links that may exist between the rate of a model reaction and the thermodynamic acido-basic properties of the surface are then discussed. These links have been investigated on a series of MgO of different morphologies and levels of hydroxylation in order to vary their basic properties [2]. Thermodynamic basicity of the surface is probed by following the deprotonation of protic molecules like methanol or propyne with IR spectroscopy. The catalytic activity on basic sites is evaluated with MBOH conversion and alkene isomerization.

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. Hydroxylated surfaces are obtained by subsequent hydration and evacuation at increasing temperature T_t. MBOH isosurface conversion experiments [2] are performed at 393 K. MBOH pressure is adjusted by a saturator at 303 K. Similarly, allylbenzene isomerization is performed at 523 K. Allylbenzene partial pressure is adjusted by a saturator at 293 K

Results and Discussion

On highly dehydroxylated surfaces the deprotonating ability of the surface is correlated with its activity in MBOH decomposition.[2] In the case of hydroxylated surfaces, the higher the hydroxylation level, the lower the deprotonating ability but the higher the reactivity. Thus in that case thermodynamic basicity is no more correlated with basic reactivity.

These results can be rationalized by considering the following MBOH decomposition reaction scheme (Figure 1)
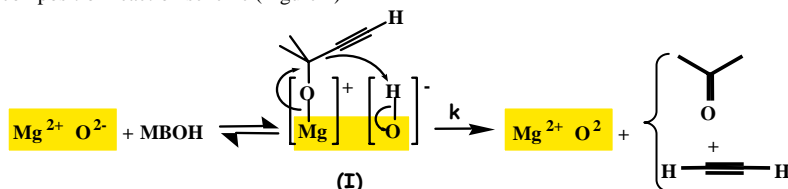

Figure 1- Proposed mechanism for MBOH conversion on basic sites

If the basic site (which is an acid-base pair) is strongly basic, the deprotonated intermediate (I) is well stabilized thus its reactivity may be lower than on a weak basic site. This behavior strongly depends on the nature of the rate determining step. In the case of alcohol reactivity, deprotonation is commonly assumed to be non-rate determining while, in the case of alkene isomerization, the reverse is usually admitted. Allylbenzene isomerization was then performed on the same hydroxylated samples and the results are given in Figure 2.
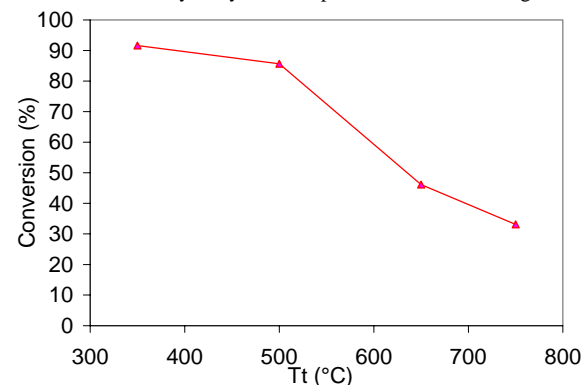

Figure 2. Allylbenzene conversion on MgO-sol-gel sample dehydroxylated at T_t

It appears that the conversion of allylbenzene follows the same trend than that of MBOH: the more hydroxylated is the surface, the more it is reactive despite a lower thermodynamic basicity.

The discussion will be made by considering that, even when deprotonation is the rate-determining step, the reactivity correlates with the nucleophilicity of the surface and not directly with the basicity.

Conclusion

This work shows that model reaction networks can be used to probe the chemical nature of the sites and to reveal their reactivity. But the correlation between reactivity and thermodynamic properties is not obvious: even in the case of alkene isomerization, the nucleophilicity of the surface must be taken into account.

Significance

This work brings some elements in the discussion concerning the role that model reaction networks can play for the characterization of the basic properties of inorganic solids.

References

1. Lauron-Pernot, H. *Catal. Rev*. 48, 315 (2006).
2. Bailly, M-L., Chizallet, C., Costentin, G., Krafft, J-M., Lauron-Pernot, H. and Che, M. *J. Catal.* 235, 413 (2005) and Chizallet, C., Bailly, M-L., Costentin, G., Lauron-Pernot, H., Krafft, J-M., Bazin, P., Saussey, J. and Che, M. *Catal. Today*. 116, 196 (2006).
3. Bailly, M-L., Costentin, G., Lauron-Pernot, H., Krafft, J-M. and Che, M. *J. Phys. Chem. B*. 109, 2404 (2005).