Role of Pretreatment and of Oxygen Vacancies on the Catalytic Behavior of ZnO Toward Alcohols Conversion: an EPR and DRIFTS Study

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Introduction and Objectives

Zinc oxide is a common white semiconductor material, used in many applications such as pigments or antiseptics, and also widely studied in optoelectronics and in heterogeneous catalysis [1]. Its catalytic properties are usually assigned either to morphology effects or to the possible influence of oxygen vacancies (V_O) [2-3]. Indeed, ZnO becomes a defective material under an oxygen deficient atmosphere. The aim of this work is to study the role of oxygen vacancies in the catalytic conversion of alcohols, exemplified by a model reaction, 2-methylbut-3-yn-2-ol (MBOH) conversion into acetone and acetylene [4] and by the conversion of ethanol. The oxygen vacancies formation depending on the conditions of the pre-treatment is followed by *in situ* and *operando* EPR. The influence of the reaction products on the stability of oxygen vacancies and the related impact on catalytic deactivation is discussed thanks to an *operando* DRIFTS study.

Results and Discussion

Two ZnO samples, commercial kadox (9 m^2g^{-1}) and ex-carbonate (issued from thermal decomposition of zinc carbonate at 773 K in the air) (22 m^2g^{-1}) were systematically pretreated at 773 K (ramp 5 $K.min^{-1}$) under inert (N_2) or oxidant (O_2, air) flows before catalytic tests as well as for *in situ* EPR measurements (spectra recorded at room temperature). The conditions of existence of oxygen vacancies of zinc oxide were studied following the increase or decrease of the EPR signal at g = 1.96 after thermal treatment under inert or oxygenated atmospheres, respectively. For both samples, the related signal was shown to be an indirect probe of oxygen vacancies: its intensity was increased / decreased upon trapping / release of the electron associated to the formation / filling of oxygen vacancy. It is also shown that oxygen vacancies created upon inert thermal treatment at 773 K can be further filled by treatment in an oxygen atmosphere at lower temperature.

For both reactions (MBOH or ethanol conversion performed in gas phase at 403 and 673 K respectively), the conversion level is controlled by oxygen vacancies concentration, as illustrated by the direct correlation between MBOH basic conversion and the EPR signal reported for both samples on Figure 1. Thus, the catalytic properties of ZnO can be tuned by the atmosphere of pretreatment with enhanced activities measured after inert pretreatment compared to oxidative conditions.[5] The reactivity inhibition after oxidative pre-

treatment is however less pronounced in the case of ethanol conversion. Indeed, from *operando* EPR experiments performed under air flow in the 338-623 K range during the cooling down step of the pretreatment, the filling of oxygen vacancies becomes really efficient below a critical temperature of about 500 K. Thus, it was concluded that the higher reaction temperature of ethanol conversion limits the impact of pretreatment atmosphere on the conversion level under oxidative atmospheres.

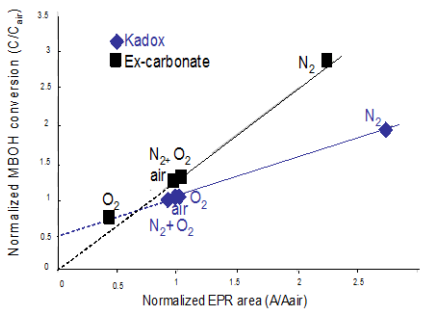

Figure 1: Variation of the MBOH conversion (T_{React}= 403 K) for kadox and ex carbonate samples versus the variation of the EPR signal (measured at room temperature) after various pretreatments: -ramp up to 773 K and cooling under air (taken as a reference), N_2, or O_2 or -ramp up to 773 K and cooling to 403 K under N_2 followed by a dwell under O_2 at 403K (N_2+O_2).

From *Operando* DRIFTS studies indicated that there was a splitting of the contributions relative to $\upsilon_{\equiv C\text{-}H}$ (3325 and 3308 cm^{-1}) and $\delta(C\text{-}(CH_3)_2)$ (1379 and 1362 cm^{-1}) of MBOH reactant on kadox sample which evidenced the existence of two different adsorption sites. The former one exists on both samples and its basicity is directly influenced by the enhanced electronic availability resulting from oxygen vacancies formation and the second one, only present on kadox sample, is a weaker basic site which is responsible for the residual activity of kadox sample in the absence of oxygen vacancies (Fig. 1).

Moreover, this *operando* characterization could also explain the two phases deactivation process observed during MBOH basic conversion that is quite rapid in the first minutes of reaction and then becomes slower. In fact, the just activated surface upon a nitrogen pretreatment exhibits acid base pairs that are efficient toward aldol condensation of the acetone formed (apparition of bands at 1437, 1419 cm^{-1} associated to diacetone alcohol), leading to the first rapid deactivation step. This polymerization is however quite rapidly inhibited. This can be assigned to the fact that the water issued of this condensation reaction dissociates on oxygen vacancies (apparition of a band at 3528 cm^{-1}), which could tune the acid-base pairs behaviour. It results in a filling of oxygen vacancies and in weakening of the strength of the sites, stopping the extension of polymerization at the benefit of the enhanced amount of acetone adsorbed on the surface (increase of the 1737 and 1725 cm^{-1} bands after several minutes of reaction). This second phase is responsible for the slow second deactivation phase observed.

Conclusions

Operando EPR and infra red are very complementary tool to evidence that the oxygen vacancies of ZnO which concentration can be tuned by pretreatment conditions govern not only the conversion level toward alcohols, but also the deactivation process.

References

[1] Halawy, S. et al J. Mol. Catal. A: Chemical, 98, L63 (1995)
[2] Mokwa, Wet al.. Surf. Sci., 117, 659 (1982).
[3] Nagao, Met al.. J. Phys. Chem., 84, 2054 (1980)
[4] Lauron-Pernot, H. Catal. Rev., 48,315 (2006)
[5] C. Drouilly, et al, FR Patent No.2 959739, assigned to IFPEN (2010)