

Understanding of the methanol partial oxidation to dimethoxymethane : study of the Re/Al₂O₃ system

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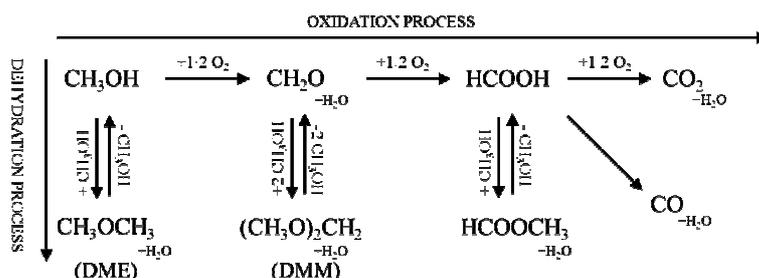
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Introduction

The rise in price of fossil fuels, the fight against global warming (Kyoto protocol), and the increase of world energy consumption strongly motivate numerous research efforts focusing on alternative products from biomass. Methanol can be obtained by steam gasification, pyrolysis, or partial oxidation of wood and agricultural waste and then be used as fuel for fuel cells [1]. Methanol can also be converted into valuable products as formaldehyde, methyl formate, dimethylether (DME) or dimethoxymethane (DMM) *via* selective catalytic oxidation (Figure 1) [2]. DMM is used in the field of fine chemicals as solvent or intermediate and is currently operational as a gasoline additive. Supported rhenium catalysts have been distinguished because of their high activities in selective oxidation of methanol to DMM [3, 4]. This reaction requires catalysts with both redox and acid functions. In order to give insights on the remarkable catalytic properties of Re-based materials, we studied the acid and redox functions of the Re/Al₂O₃ system. We focused our work on the acidity function of the support: for this, we modulated the acidity of the Al₂O₃. To complete this study, XPS has been used to probe the redox functions of the catalyst.

Figure 1: Methanol oxidation/dehydration pathways [2]



Experimental

The alumina were synthesised by sol-gel process. After drying, four samples were calcined at four different temperatures (600, 800, 1000 and 1200 °C) to obtain different alumina phases which exhibit various acidity. Rhenium catalysts deposited in these supports were obtained by manually grinding particles of metallic Re with Al₂O₃ in an agate mortar. The resulting mixture was then calcined under pure O₂ flow up to 400°C (heating rate: 1°C.min⁻¹) to oxidize the rhenium and get a well-dispersed oxide surface covering.

Surface areas of the samples were measured by a BET nitrogen adsorption method at 77 K using an ASAP 2010 machine. Redox functions of the rhenium XPS spectra were measured on a Escalab 220 XL (VG Scientific) using Al K α radiation (1286.6 eV) after 1 h at 240 °C in He/CH₃OH. In order to quantify the number of acid sites on the different alumina, TPD-NH₃ desorption was performed using a Micromeritics Autochem 2920 apparatus equipped with an on-line mass spectrometer.

Catalysts activities in methanol oxidation reaction were assessed in a fix-bed reactor. The reaction feed is composed of 7,5%mol CH₃OH, 15,5%mol O₂ in helium passing through the catalyst at a GHSV of 26000 mL h⁻¹ g⁻¹. Reactants and products were analysed with an on-line gas chromatograph (SRA) equipped with two columns (U plot, Molecular sieves) and two TCD.

Results and Discussion

XPS datas collected after He/CH₃OH treatment showed the presence of Re⁴⁺ at the Al₂O₃ surface (Table 1). Since the conversion of methanol to formaldehyde is a two electrons oxidation, we propose that the redox rhenium couple Re⁶⁺ ↔ Re⁴⁺ is involved in this reaction.

Table 1: Study of Re/Al200 redox functions by XPS spectroscopy

Treatment	Re 4f _{7/2}	BE (eV)	FWHM (eV)	%
Dehydrated	7+	46.3	2.4	87
	6+	43.5		13
After He/CH ₃ OH	7+	46.0	2.2	47
	6+	43.8		18
	4+	42.7		35

Comparing the catalytic datas obtained with the four Re/Al₂O₃ samples and the results of the TPD-NH₃ desorptions, we have evidenced that the ratio "DMM yield/DME yield" increases when the number of acid sites on the alumina support decreased (Figure 2). This result shows that the acid sites of the support lead to the formation of DME meanwhile the rhenium acidity leads to the formation of DMM.

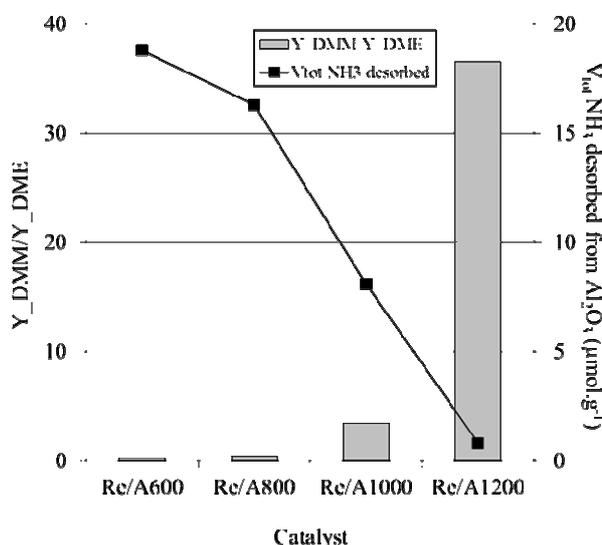


Figure 2: Correlation between the catalytic results and the number of acid sites determined by TPD-NH₃

Conclusion

We propose this following mechanism for the conversion of methanol to DMM on Re/Al₂O₃ system: the redox couple Re⁶⁺ ↔ Re⁴⁺ is responsible for the oxidation of methanol to formaldehyde, while the acidity of Re is appropriate for the conversion of formaldehyde to DMM. The acid sites on Al₂O₃ are in competition with the Re acidity and lead to the formation of DME.

References

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