DME production from methanol dehydration over boria modified alumina

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Introduction

Dimethyl ether (DME) is regarded as a multi-purpose fuel for 21st century as it can find application in power generation, LPG alternative and transportation fuel in substitution to diesel. Nowadays, DME use has been limited to CFC replacement. The modern approach involves the one-step transformation $CO/H_2 \rightarrow$ DME over bi-functional catalysts that associate hydrogenation and typical methanol dehydration sites. It is known that proposed catalysts are mainly based on Cu-Zn/γ-Al_2O_3. The creation of these hydrogenation sites (Cu, Zn) onto γ-Al_2O_3 surface may cause a diminishment in the number of acid sites available for the dehydration step. Enhancement of the acid strength seems an interesting way to overcome this problem. By modifying the acid properties of alumina, the catalytic activity is expected to be kept. According to the literature[1-4], addition of B_2O_3 to Al_2O_3 leads to a mixed oxide with increased acid character. In this study we evaluate the effects in methanol dehydration caused by boron incorporation in γ-Al_2O_3.

Results and Discussion

AlB was prepared by co-precipitation method using boric acid and aluminum nitrate solutions, with NH_4OH as precipitant. γ-Al_2O_3 was also prepared as reference.10% and 33% boria catalysts (Al10B, Al33B) presented poor crystalline patterns by XRD. Al33B sample diffractogram showed the formation of aluminum borate. Higher boria loadings and calcination temperatures result in little loss of surface area (Tab.1). IR spectroscopy analysis in the OH stretching vibration region showed that boron addition caused basic Al-OH groups (at around 3745 cm^{-1}) to almost disappear. A broadening of the band at 3680 cm^{-1} was observed and it could be assigned to the contribution of B-OH vibration[4]. Concerning the acidic characteristics, pyridine adsorption experiments on AlB samples revealed the presence of typical alumina Lewis acid sites. These sites are represented by the IR peaks at 1613 cm^{-1} and 1595 cm^{-1} resulting from pyridine coordinatively bonded to the surface. Comparison with pure alumina (Al-I) indicated that the number of Lewis sites was not significantly changed. Still, thermal desorption showed that modified alumina has greater acid strength. The presence of a band at 1545 cm^{-1} (interaction with Brönsted acid sites) is not unequivocal as B-O bond vibrations in BO_3 and BO_4 units are characterized by broad absorptions in 1500-1200 cm^{-1} and 1100-900 cm^{-1} regions, respectively. The generation of Brönsted acid sites is still controversial[1,4], but it seems to be highly dependant of boron content. CO_2 adsorption was also conducted to evaluate the catalysts basic sites. As can be seen by direct comparison with Al-I, shown in fig. 1, these sites diminished sharply (1655cm^{-1}, 1445cm^{-1}). This figure also presents an additional spectrum of a sample prepared by impregnation (Al10B-I_{imp}) which greatly evidences this effect. By modifying alumina with boria, we observed that catalytic performance is negatively affected, as shown by the temperature at which the conversion achieved 30% (Tab.1). It could be explained by the disappearance of the required basic sites that was evidenced by CO_2 adsorption. Methanol dehydration can be used to characterize acidity as it proceeds either on Lewis acid/base or Brönsted acid sites. As AlB catalysts still demonstrated reasonable DME yields, it would then indicate that the reaction took place mainly via Brönsted mechanism. The overall activity could thus suggest that a suitable acidity was not accomplished. DME synthesis is indeed readily conducted over zeolites due to their strong Brönsted acid sites. However, hydrocarbons can be obtained at methanol synthesis temperatures, which may hinder their application in DME direct synthesis (one-step reaction).

On the other hand, AlB solids might bring about the possibility to control the strength of active sites by improving preparation methods and obtain adequate boria/alumina ratio. Consequently, hydrogenation sites could be created by deposition methods over a tailor-made surface containing suitable acid centers allowing its successful use in the one-step process.

Table 1 – Characteristics of AlB catalysts

Sample	Surf. area (m^2/g)	Crystal structure	T at 30% conversion
Al10B-I[a]	279	γ-Al_2O_3	199°C
Al10B-II[b]	211	γ-Al_2O_3	218°C
Al33B-I	202	γ-Al_2O_3, $9Al_2O_3.2B_2O_3$	227°C
Al33B-II	118	$9Al_2O_3.2B_2O_3$	252°C
Al10B-I_{imp}	250	γ-Al_2O_3	209°C
Al-I	252	γ-Al_2O_3	191°C

[a] I=calcination at 500°C, [b] II=calcination at 800°C

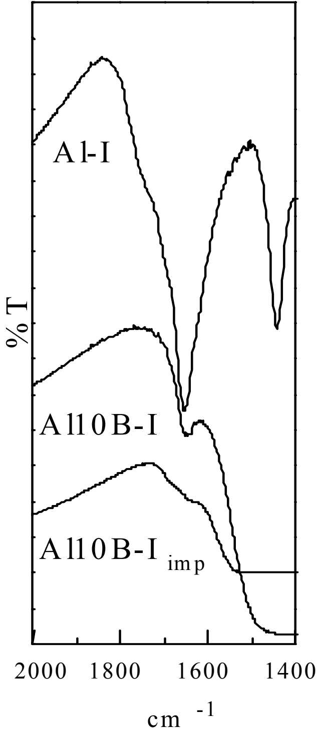

Figure 1 – IR spectra after CO_2 adsorption

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