Synthesis of mixed alcohols over Ni-modified alkali-doped molybdenum sulfide catalysts prepared by conventional coprecipitation and by microemulsion: Effect of alcohols co-feeding

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Introduction

Syngas can be obtained from biomass and a wide variety of waste products and then catalytically converted to mixed alcohols, which are a promising alternative to conventional fuels. Sulfided molybdenum-based catalysts promoted with alkali and transition metals are one of the most interesting catalysts since they are sulfur resistant and deactivate slowly by coke deposition [1]. The microemulsion technique appears to be a suitable method to manufacture the catalyst considering it has shown enhanced properties in many applications when compared with conventional techniques [2].

Moreover, it has been reported that higher alcohols yield can be enhanced by co-feeding methanol and ethanol with the syngas [3]. However, to the authors' knowledge, little is known regarding this effect over K-Ni-MoS_2 catalysts.

The aim of this work is to develop and study the performance of a novel Ni-modified alkali-doped molybdenum sulfide catalyst prepared by using the microemulsion technique and compare it with conventional catalysts. The effect of alcohols co-feeding will also be studied.

Materials and Methods

Three different conventional catalysts were prepared (containing one or both promoters). Nickel promotion was done by coprecipitation of $Ni(CH_3COO)_2$•$4H_20$ and $(NH_4)_2MoS_4$ solutions. Potassium doping was achieved by a mechanical mixing. The final catalysts were obtained after thermal decomposition at 450°C under H_2 atmosphere and crushing/sieving to a pellet size of 45-250 µm. In order to synthetize the microemulsion (ME) catalyst, two analogous water-in-oil systems were mixed, containing the nickel and molybdenum salts. The rest of the preparation procedure is analogous to that used for the conventional catalysts: alkali doping, H_2 treatment, crushing and sieving.

Catalysts were characterized by means of ICP, XPS, nitrogen adsorption measurements and XRD. Activity and selectivity tests were performed in a setup described in detail elsewhere [4]. Briefly, CO hydrogenation reactions were performed with a premixed syngas (H_2/CO ratio=1/1 and 4% N_2 as internal standard) at P=91 bar, T=340/370°C, GHSV=2000-14.000 mL/ h•gcat. Product analysis was carried out with an on-line GC, equipped with a TCD and two FID detectors. Activity and selectivity data were measured on stable catalysts, after at least 100 h on stream.

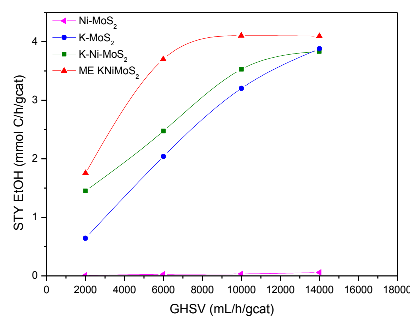
Results and Discussion

The ME catalyst shows a greater enrichment of the promoters, especially potassium, on the surface, as can be seen in **Table 1.**

Table 1. Physicochemical properties of conventional and ME K-Ni-MoS_2 catalysts.

Catalyst	ICP ratios		XPS ratios		BET SA (m^2/g)	BJH ads. pore volume (cm^3/g)	BJH ads. avg. pore diameter (Å)
	Ni/Mo	K/Mo	Ni/Mo	K/Mo			
K-Ni-MoS_2	0.5	1.2	0.1	2.4	3.2	2,53 10^{-2}	311
ME K-Ni-MoS_2	0.4	1.5	0.4	14	1.3	6,05 10^{-3}	328

Regarding the catalytic tests, the combination of both promoters is essential to achieve high selectivities to ethanol and higher alcohols. In addition, the activity of the novel ME catalyst is higher at the different space velocities and reaction temperatures studied within this work. Space-time yield of alcohols and, specifically, of ethanol is also enhanced with the new preparation method, as can be seen in **Figure 1**. The stability of the ME catalyst has also been examined and no significant deactivation was observed after about 200 h on stream **(Figure 2)**.



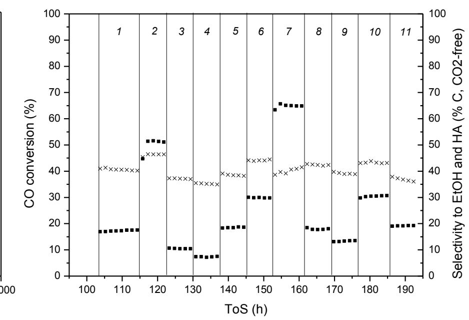


Figure 1 [left]. Space-time yield of ethanol for the different catalysts, at T=340°C (right).
Figure 2 [right]. CO conversion (■) and selectivity (□) to higher alcohols vs ToS for the ME catalyst, at the following conditions: T(°C)=340 (1-5,11) / 370 (6-10); GHSV(mL/h•g_{cat})=2000 (2,7) / 6000 (1,5,6,10,11) / 10000 (3,8) / 14000 (4,9).

Significance

The novel sulfided molybdenum-based catalyst, prepared by the microemulsion technique, improves the catalytic conversion of syngas to mixed alcohols. Work is on-going regarding the effect of alcohols co-feeding in the system.

References

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