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ALKALI/TX₂ CATALYSTS FOR CO/H₂ CONVERSION TO C₁-C₄ ALCOHOLS

Technical Progress Report for the Period

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ALKALI/TX₂ CATALYSTS FOR CO/H₂ CONVERSION TO C₁-C₄ ALCOHOLS

OBJECTIVE AND SCOPE OF WORK

The objective of this research is to investigate and develop novel catalysts for the conversion of coal-derived synthesis gas into C₁-C₄ alcohols by a highly selective process. Therefore, the variations of catalyst activity and selectivity for the synthesis of alcohols from H₂/CO ≤ 1 synthesis gas for a series of A/TX₂ compounds, where A is a surface alkali dopant, T is a transition metal, and X is a S, Se, or Te, will be determined. The alkali component A, which is essential for C-O and C-C bond forming reactions leading to alcohols, will be highly dispersed on the TX₂ surfaces by using chemical vapor deposition (CVD) and chemical complexation/anchoring (CCA) methods.

The target alcohol space time yields are of the order of 1 kg of alcohol product per kg of catalyst per hour and the target selectivity is > 90% to alcohols. Among the A/TX₂ compounds initially investigated, preference will be given to A = Cs, T = Group VB element (V, Nb, Ta), and X = S or Se. So delimited A/TX₂ catalysts possess the strongest base (Cs), and the CCA preparation method using crown ethers is expected not only to disperse the alkali ions atomically but also to enhance the basicity of their counterions, thus further increasing the specific rates of the base-catalyzed C-O and C-C bond forming reactions.

The benefit of this research rests in providing a scientific foundation and a database for catalytic processes leading to high octane oxygenated fuels such as ethanol/methanol/propanol mixtures, as well as to low olefins obtained by further catalytic dehydration of the C₂-C₄ alcohols. Since the source of carbon can be coal-derived synthesis gas, this research will make a contribution to the technology for high quality clean transportation fuels and for basic chemicals from coal.

ALKALI/TX₂ CATALYSTS FOR CO/H₂ CONVERSION TO C₁-C₄ ALCOHOLS

SUMMARY OF TECHNICAL PROGRESS

Ruthenium disulfide catalysts have been synthesized, tested, and characterized during this period of research. It was observed that both the undoped and Cs-doped RuS₂ catalysts produced alcohols and lower amounts of hydrocarbons from H₂/CO = 1.0 synthesis gas at temperatures above 300°C. Calcination and catalytic testing resulted in partial reduction of the RuS₂ to Ru⁰. Calcination under H₂S prevented the partial reduction of the RuS₂ catalyst, but subsequent catalytic testing again resulted in the formation of a quantity of Ru⁰. A Cs-doped RuS₂ catalyst was prepared, but it might have has too high of a loading of Cs. Upon testing, a lower activity was observed for the doped catalyst compared with the undoped catalyst, but the alcohol selectivity was the same for the two catalysts.

TECHNICAL PROGRESS

Preparation of RuS₂-Based Catalysts

Preparations of RuS₂ and Cs/RuS₂ catalysts were carried out using dry-box techniques for precipitation of RuS₂ from a non-aqueous solvent. The procedure for preparation of the RuS₂ can be illustrated by equation 1, where the reaction is carried out under dry, non-aqueous, anarobic conditions.

The NH₄SH reactant is prepared via the reaction of H₂S and NH₃ at dry ice temperature, and it is then dissolved in methanol. The sequence of steps in the preparation process is given below:

1. Preparation of NH₄SH At dry ice temperatures, ≈4 g of H₂S(g) is liquified and titrated with NH₃(g) to precipitate NH₄SH as a white crystalline solid. This step is repeated until 20 g NH₄SH is collected in a 100 ml round bottom flask.
2. Dissolution of NH₄SH Approximately 100 ml dry methanol is added to the flask containing NH₄SH until all of the solid is dissolved.
3. Dissolution of RuCl₃ In a nitrogen filled glove box, ≈20 g of RuCl₃ is placed in a 1 l round bottom flask. Dry methanol (50 ml) is then added to the flask until the RuCl₃ is partially dissolved.
4. Reaction of RuCl₃ and NH₄Cl The NH₄SH-CH₃OH solution is transferred into the 1 l flask containing the partially dissolved RuCl₃. Approximately 16 g of RuS₂ is formed as a precipitate, which is then digested for 16 hr prior to decantation, washing with methanol, and drying.

Doping of the RuS₂ was carried out by an impregnation technique using an evacuated glass apparatus that was employed in our earlier studies of alkali-doped MoS₂ catalysts [1,2]. A 2.5 g portion of the RuS₂ was placed

in the vacuum apparatus and evacuated at 110°C for 2 hr. Doping was then carried out in a stepwise procedure under an inert atmosphere using additions of 0.5346 M CsOOCH solution to the RuS₂. After the doping procedure was completed, the catalyst was evacuated overnight at ambient temperature.

Catalytic Testing of the RuS₂-Based Catalysts

Testing of the catalysts was carried out at 82.7 MPa in the temperature range of 250 to 355°C with H₂/CO = 1 synthesis gas at GHSV = 7750 l/kg catal/hr. The RuS₂ catalyst (1.000 g diluted with Pyrex beads) did not exhibit hydrocarbon activity at temperatures less than 300°C, as the undoped MoS₂ catalyst did. For example, at 295°C and 82.7 MPa with H₂/CO = 0.96 at GHSV = 7775 l(STP)/kg catal/hr, the MoS₂ catalyst produced 193 g of hydrocarbons (46 wt% CH₄), along with 2.75 g of methanol/kg catal/hr [3]. Under the same conditions, the undoped TaS₂ produced 7 g of hydrocarbons/kg catal/hr and no alcohols [4].

With the RuS₂ catalyst, as the temperature was increased above 300°C, methanol was begun to be formed. The yields of the products observed over the RuS₂ catalyst are shown in Figure 1 for the temperature range of 305-355°C. Methanol was the principal product, but it is clear that the yield of methane was parallel to that of methanol. On a carbon atom %, the selectivities of methane and methanol approached 1/1 at the higher temperatures, as shown in Figure 2. In Figure 1, it is indicated that the product yields did not increase when the temperature was increased from 345°C to 355°C. Therefore, the reaction was allowed to run at the higher temperature for 34 hr, and then the reaction temperature was lowered to 315°C and maintained at that temperature for 15.5 hr. Figure 3 shows that the catalytic yields did not significantly decrease at either temperature as

would be expected if extensive sintering were occurring. In deed, the methane yield was higher at 315°C after the higher temperature testing than it was prior to the more extensive testing.

The 2% Cs/RuS₂ catalyst (0.9146 g) was also tested for the synthesis of alcohols and hydrocarbons at the same pressure and GHSV with H₂/CO = 1.0 synthesis gas. The activities observed at 315 and 325°C are shown in Figure 4. The Cs-doped catalyst was less active than the undoped RuS₂, which might be due to over-doping of the catalyst. For both the Cs-doped and undoped RuS₂, the alcohol selectivity in this temperature range was ≈65% on a carbon atom basis or ≈80 wt%.

Characterization of the RuS₂ and Cs/RuS₂ Catalysts

All of the catalysts and their precursors that were prepared in this study were examined by X-ray powder diffraction (XRD). Figure 5 illustrates the XRD pattern obtained for RuS₂ after it was prepared and dried, and it is evident that this material possessed little crystallinity. After calcination of this sample under N₂ at 550°C for 2 hr, the RuS₂ increased it's crystallinity to an average crystallite size of 14.5 nm. However, as indicated in Figure 6, diffraction lines corresponding to metallic ruthenium were also observed. This demonstrated that a portion of the RuS₂ was reduced to Ru⁰ during the calcination procedure.

A second portion of the amorphous RuS₂ precursor was calcined using the same procedure but with an atmosphere of H₂S rather than N₂. As shown in Figure 7, the RuS₂ again crystallized to form small particles, but no diffraction peaks assignable to Ru⁰ were observed. After testing this sample for catalytic activity towards the formation of alcohols and hydrocarbons for ≈150 hr, the diffraction pattern shown in Figure 8 was obtained. This pattern is very similar to that shown in Figure 6, which

demonstrates that the catalyst was partially reduced during the testing procedure using $H_2/CO = 1$ synthesis gas. It is clear that the diffraction lines corresponding to Ru^0 are appreciably narrowed for the tested sample compared with the untested catalyst, indicating that the Ru^0 crystallite size increased by nearly a factor of three. The crystallite sizes were calculated from the diffraction patterns using the Scherrer equation:

$$L_c = 0.9/(W_x - \omega')\cos\theta,$$

where L_c - the crystallite size, W_x - the observed peak width at half peak height, ω' - the observed peak width for highly crystalline material (instrumental broadening), and θ - the angle between the incident and diffracted beams. The calculated crystallite sizes (in nm) are tabulated in Table 1.

TABLE 1

Calculated Crystallite Sizes (nm) for RuS_2 and Ru^0 .

<u>Diffraction Peak</u>	RuS_2				Ru^0	
Degrees (2θ)	27.4	31.7	35.5	45.5	42.0	43.9
Miller Indices	111	200	210	220	002	101
RuS_2 , N_2 Calcined	14.2	14.6	11.8	14.6	12.8	17.0
RuS_2 , H_2S Calcined	10.5	12.7	13.3	14.2	--	--
RuS_2 , Tested After H_2S Calcination	10.1	12.4	11.8	12.2	36.3	32.3
RuS_2 , Untested 2% Cs Doped	16.3	18.6	19.4	12.8	30.5	30.0
RuS_2 , Tested 2% Cs Doped	18.6	16.3	16.4	14.2	26.3	21.9

X-Ray Photoelectron Spectroscopy (XPS) measurements were obtained for the catalysts before and after testing. Spectral lines were obtained at the expected positions for Ru ($3s$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, $3d_{5/2}$) and for S ($2s$,

2p). In addition, lines attributable to oxygen were also present in every spectrum. Therefore, it is evident that oxygen readily adsorbed on the surface of RuS_2 during the transfer of the samples into the XPS instrument. A distinction of Ru^0 from Ru^{4+} could not be made, and no clear line assignable to a sulfate species was observed.

Diffraction patterns were also obtained for the untested (calcined under a N_2 atmosphere) and tested samples of the 2% Cs/RuS_2 catalysts, and they are shown in Figures 9 and 10. In both cases, strong diffraction lines corresponding to Ru^0 were present, and the calculated crystallite sizes are given in Table 1.

References:

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3. Reference 1, p 59.
4. K. Klier, R. G. Herman, and R. Bastian, "Alkali/ TX_2 Catalysts for CO/H_2 Conversion to $\text{C}_1\text{-C}_4$ Alcohols," Technican Progress Report DOE/PC/88933-1 (December 1988).

UNDOPED RuS_2 : PRODUCT YIELDS

FIGURE 1

UNDOPED RuS₂ SELECTIVITY

FIGURE 2

UNDOPED RuS_2 : PRODUCT YIELDS

FIGURE 3

2% Cs-DOPED RuS₂: PRODUCT YIELDS

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

Sample: RUS2C File: RB15.SM

FIGURE 8

FIGURE 9

FIGURE 10

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