ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

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OBJECTIVE AND SCOPE OF WORK

The objective of the proposed research is to investigate and develop a novel catalytic process for the conversion of coal-derived synthesis gas into high octane C_1 - C_4 alcohols, especially ethanol, by a highly selective and efficient pathway.

The catalysts chosen fall into the general category of bifunctional, base-hydrogenation, sulfur-tolerant chalcogenides with a heavy alkali (K^+ , Rb^+ , Cs^+) component dispersed on their surfaces. The alkali base activates CO and CO_2 by an associative mechanism that does not rupture the C-O bond and the transition metal chalcogenide, primarily sulfide, activates hydrogen for the reduction of HCO_x intermediates (viz. formate $HCOO^-$) to alcohols. The combination of the two functions also greatly promotes the water gas shift (WGS) reaction, and a novel class of low temperature, sulfur-tolerant WGS catalysts ensues. Different sulfides possess different hydrogen activation ability, viz. $RuS_2 > MoS_2 > NbS_2$. The product alcohols are potential precursors of undesired hydrocarbons (e.g. methanol of methane) and actually not the highest but rather optimum hydrogenation ability of the catalyst is desired. An important guide to finding such an optimum is reaction kinetics, particularly with respect to hydrogen, which is proposed to be investigated here along with establishing selectivity patterns in the presence of CO_2 , H_2O , and H_2S (Tasks 1 and 2). The water gas shift (WGS) process, which is operated under less severe conditions than the alcohol synthesis, also requires a balance between the basic and hydrogenation/dehydrogenation function, including hydride abstraction from the formate $HCOO^-$, and the optimum balance between the two functions for WGS and alcohol synthesis is generally different. It is proposed to establish

the optimum process conditions and catalyst compositions for WGS and alcohol synthesis in terms of reaction pressure, temperature, and alkali/TS₂ ratio for T = Nb, Mo, and Ru (Task 3).

The above tasks are greatly assisted by solid state and spectroscopic investigations of the catalyst and the surface intermediates (Task 4), including the highest available resolution valence band XPS spectroscopy, which is carried out in the SCIENTA ESCA-300 laboratory at Lehigh University. Other instrumental techniques that will be utilized include X-ray powder diffraction, Auger spectroscopy, SEM, HR-TEM, FTIR, NMR, and optical DRS, including exciton spectroscopy.

The impact of the current research promises to be (i) to develop a novel process for ethanol, (ii) to develop a novel low temperature sulfur-resistant WGS catalyst and process, (iii) to establish kinetic laws for the above processes, and (iv) to determine patterns and modes of activation of the reaction components, as well as gaseous promotes, such as CO₂, H₂O, and H₂S, on the rates and selectivities of the WGS and alcohol synthesis processes. The alcohol fuel so produced can also be converted, partially or totally, to high octane ethers, e.g. ethanol to ETBE. Therefore, the proposed research is directed to the synthesis of an alternative clean high octane liquid fuel in which all carbon originates from coal.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

SUMMARY OF TECHNICAL PROGRESS

New RuS_2 and NbS_2 catalysts have been prepared, and these have been surface doped with Cs. Characterization of these materials has been carried out by X-ray powder diffraction and BET surface area measurements, and they have been tested for hydrocarbon and alcohol synthesis activity in the temperature range of 275-325°C and at ≈ 82 atm pressure with $\text{H}_2/\text{CO} = 1$ synthesis gas.

Under the reaction conditions employed to-date, the RuS_2 catalysts are much less active than were the MoS_2 -based catalysts. The RuS_2 catalysts were much more crystalline than the MoS_2 catalysts and have a different crystal structure. Less crystalline, or even amorphous, RuS_2 catalysts need to be prepared and tested.

Preparation of the niobium sulfide catalysts by a variety of methods resulted in sub-stoichiometric materials, e.g. as prepared from the elements, the bulk stoichiometry was found to be $\text{NbS}_{1.84}$ by elemental analysis but a surface stoichiometry of $\text{NbS}_{2.01}$ by X-ray photoelectron spectroscopy analysis.

Purchased samples of niobium sulfide were also found to be sub-stoichiometric materials. Catalytic testing of these materials resulted principally in the formation of hydrocarbons, mainly CH_4 , and CO_2 from $\text{H}_2/\text{CO} = 1$ synthesis gas. These catalysts did not exhibit appreciable activity and the yields were < 2 g/kg catal/hr, e.g. the $\text{Cs}/\text{NbS}_{1.4}$ catalyst was ≈ 20 less active per unit surface area as the Cs/MoS_2 catalyst.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS - PART 1

Discussion of H₂/CO Ratios

The object of this project is to develop a novel catalytic process for the conversion of coal-derived synthesis gas into high octane C₁-C₄ alcohols. The catalysts under consideration are the bifunctional transition metal dichalcogenides (specifically, disulfides) with a heavy alkali (K⁺, Rb⁺, Cs⁺) component dispersed on their surfaces. The purpose of the alkali base is to activate the CO without rupture of the C-O bond. Activation of hydrogen occurs on the transition metal disulfide, TS₂, surface. Both alcohol formation and the water-gas shift reaction are promoted by the combination of these two functions.

The effect of the H₂/CO reactant ratio on the production of alcohols was investigated thermodynamically. At the present time, coal gasifiers produce synthesis gas with an H₂/CO ratio between 0.5 and 1.1. The ideal catalyst would produce C₁-C₄ alcohols using a reactant ratio in this range. The ratio of H₂/CO obtained from the chemical equation (2) for production of alcohols is 2. However, the water-gas shift reaction, (1), if present will reduce the H₂/CO ratio necessary for alcohol formation. If the catalyst is a good water-gas shift catalyst, then this reaction will use up some of the reactant CO and H₂O produced upon alcohol formation to form CO₂ and H₂. Since the ratio of the reactant gases, H₂/CO, under study will be approximately 1, this ratio is actually CO rich and H₂ deficient. Thus promotion of the water-gas shift (WGS) reaction will enhance the amount of H₂ present. A general chemical equation for the formation of a C_n linear alcohol is shown in (2) below. The ideal ratio of H₂/CO is 2 for all C_n alcohols. However, if the WGS reaction removes all of the water produced upon formation of the C_n alcohol then the H₂/CO ratio is reduced from its ideal value of 2. As the number of carbons (n) increases in the C_n alcohol, the H₂/CO ratio decreases (shown in (3) and Table 1). Thus for a catalyst with a great deal of WGS activity, lower H₂/CO ratios favor the formation of higher alcohols.

Table 1.
Ideal H_2/CO ratio for the production of linear C_n alcohols assuming the WGS reaction removes all of H_2O produced.

<u>Alcohol</u>	<u>n</u>	<u>H_2/CO ratio</u>
Methanol	1	2.000
Ethanol	2	1.000
Propanol	3	0.800
Butanol	4	0.714
Pentanol	5	0.667
Hexanol	6	0.636

Hydrocarbon formation occurs to a significant extent over the undoped MoS_2 catalysts. Thus the effect of varying the H_2/CO ratio must also be considered in terms of hydrocarbon formation. The general reaction of CO and H_2 to produce linear C_n hydrocarbons is shown in (4) and the H_2/CO ratios in Table 2. As the number of carbons, n, increases the ratio of H_2/CO decreases to a limiting value of 2, the same value for linear alcohol formation without WGS. Thus with no WGS reaction, lower ratios of H_2/CO favor the formation of alcohols over the formation of hydrocarbons. Linear hydrocarbon formation with removal of all H_2O by the WGS reaction is shown in (5) and Table 3.

Table 2.
Ideal H_2/CO ratios for linear hydrocarbon formation without removal of H_2O by the WGS reaction.

<u>Hydrocarbon</u>	<u>n</u>	<u>H_2/CO ratio</u>
Methane	1	3.000
Ethane	2	2.500
Propane	3	2.330
Butane	4	2.250
Pentane	5	2.200
Hexane	6	2.167

Removal of the H_2O produced on formation of the linear hydrocarbon or alcohol by the WGS reaction lowers the H_2/CO ratio necessary for reaction. However, on comparing the H_2/CO ratios needed when the WGS is taken into consideration for the same number of carbons, n, lower ratios favor the formation of hydrocarbons. From the above discussion, a few trends can be noted. For a catalyst on which the WGS reaction does not occur to a significant extent the ratio of H_2/CO should be at least 2 for production of alcohols. This ratio favors alcohol and higher C_n hydrocarbon production. For a catalyst on which the WGS reaction occurs to a significant extent (for instance Cs/MoS_2), the ratio of H_2/CO should be ≤ 2 . The smaller the ratio the more favorable the formation of both higher

C_n hydrocarbons and alcohols. The initial ratio of H₂/CO proposed for use on the catalysts under investigation is ~ 1. This ratio favors both the formation of methane and ethanol when the WGS reaction is significant.

Table 3.

Ideal H₂/CO ratios for linear hydrocarbon formation with removal of H₂O by the WGS reaction.

<u>Hydrocarbon</u>	<u>n</u>	<u>H₂/CO ratio</u>
Methane	1	1.000
Ethane	2	0.750
Propane	3	0.667
Butane	4	0.625
Pentane	5	0.600
Hexane	6	0.583

Previous Investigations

The transition metal disulfide, MoS₂, was studied previously for the formation of C₁-C₄ alcohols from synthesis gas, H₂/CO ~ 1, under high pressures, 81.6 atm. The most active catalyst for the formation of alcohols was found to be Cs doped MoS₂.¹ Undoped MoS₂ produced mainly hydrocarbons with small amounts of alcohols, while Cs-doped MoS₂ produced large amounts of methanol and small amounts of hydrocarbons. Preliminary work on doped and undoped RuS₂ has shown no significant activity toward the formation of hydrocarbons or alcohols.

MoS₂ catalysts studied previously were prepared from the thermal decomposition of molybdenum trisulfide, MoS₃.¹ The MoS₂ catalyst resulting from this type of preparation is stoichiometric, semicrystalline in nature, and possesses a BET surface area of ~ 60 m²/gm. Alkali doping of the MoS₂ was carried under vacuum with an aqueous solution of the alkali salt (e.g. CsCOOH).

Present Research with RuS₂

RuS₂ catalysts were prepared using the method of Pecoraro and Chianelli.² Ruthenium chloride, α-RuCl₃, and lithium sulfide, Li₂S, were mixed together in a solution of methanol for an extended period. The amorphous ruthenium sulfide resulting from this reaction is pyrophoric, thus the whole procedure was carried out in an inert atmosphere. Crystalline RuS₂ was obtained by sulfiding the amorphous product with 14.8% H₂S/H₂ at 500° C. The RuS₂ obtained from this type of preparation is stoichiometric, highly crystalline in nature and possesses a low surface area of ~ 8

m²/gm. A methanolic solution of CsCOOH·xH₂O was used to dope the catalyst in an inert atmosphere.

A comparison of the catalysis occurring over undoped and doped MoS₂ and RuS₂ is shown in Table 4. The doping level of the MoS₂ catalyst was 15% Cs/MoS₂ while that for RuS₂ was 0.4% Cs/RuS₂. As indicated in Table 4, undoped MoS₂ exhibited a certain amount of catalytic activity toward the formation of hydrocarbons at a temperature of 295° C. Undoped RuS₂ did not exhibit much catalytic activity since the conversion was very low, 0.16 mol CO/kg cat-hr. The low conversion was not just an effect of the smaller surface area of RuS₂. If the difference in surface areas is taken into account, the conversion of RuS₂ should be multiplied by 7.5 (60 $\frac{\text{m}^2}{\text{gm}}$ / 8 $\frac{\text{m}^2}{\text{gm}}$), a conversion of ~ 1.2 mol CO/kg cat-hr results. Thus, the surface areas alone can not account for the lower conversion of the RuS₂ catalyst.

Table 4.
Comparison of the products obtained upon catalytic testing of undoped and Cs-doped MoS₂ and RuS₂.
(Yields and conversions for MoS₂ catalysts obtained from ref. 1)

<u>Temperature</u>	<u>Catalyst</u>	<u>Yields</u> ($\frac{\text{g}}{\text{kg cat-hr}}$)	<u>Conversion</u> ($\frac{\text{mole CO}}{\text{kg cat-hr}}$)
320° C	RuS ₂	7.1 (CO ₂) 1.0 (CH ₄)	0.16
320° C	Cs/RuS ₂	7.7 (CO ₂) 1.0 (CH ₄)	0.11
295° C	MoS ₂	89.11 (CH ₄) 48.33 (C ₂ H ₆ , C ₂ H ₄) 31.79 (C ₃ H ₈ , C ₃ H ₆) 2.75 (CH ₃ OH) 135.69 (H ₂ O)	13.06
285° C	Cs/MoS ₂	44.65 (CH ₄) 8.63 (C ₂ H ₆ , C ₂ H ₄) 2.68 (C ₃ H ₈ , C ₃ H ₆) 191.44 (CH ₃ OH) 96.34 (C ₂ H ₅ OH) 28.00 (C ₃ H ₇ OH) 2.82 (H ₂ O)	14.85

Doping of the MoS₂ catalyst with CsCOOH resulted in a shift of the products from mainly hydrocarbons to alcohols. The overall conversion of CO also increases from 13.06% to 14.85%. The WGS reaction begins to play a more important role in the catalysis since the amount of H₂O being produced decreased upon doping. The catalytically active sites on the Cs/MoS₂ system have been studied widely in the literature. Since MoS₂ has a layer structure, the basal plane is generally believed

to be inert. The catalytic activity is thought to occur on exposed edge planes where unsaturated S and Mo atoms exist.

The reason for the lack of activity of the RuS_2 catalysts is under investigation. As mentioned previously, the RuS_2 catalysts as prepared in this study were highly crystalline in nature. Thus, the number of unsaturated Ru and S atoms exposed on the surface is small. If the chemistry of alcohol formation occurs through some type of coordinatively unsaturated metal or sulfur surface atoms, then highly crystalline, stoichiometric systems may not have enough unsaturated sites for catalysis to occur. A logical next step in the study of the RuS_2 system would be to study the catalytic activity of the amorphous ruthenium sulfide. The amorphous solid is of higher surface area than the highly crystalline RuS_2 obtained after pretreatment. Pretreatment of the amorphous ruthenium sulfide in pure nitrogen or H_2/N_2 environment could also lead to a system that may have sulfur vacancies, potential sites for catalytic activity. The catalytic activity of these nonstoichiometric forms of ruthenium sulfide can then be compared to the stoichiometric RuS_2 to determine the effect of sulfur vacancies.

References

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TECHNICAL PROGRESS-PART 2

Experimental

Preparation from the Elements

The niobium sulfide catalyst preparation from the elements has been described in a previous quarterly report.¹

Purchased Samples

Two samples were purchased from chemical companies for characterization, comparison and catalytic testing. The first sample was purchased from Alfa Chemical Company (catalog no. 13099). The sample was pretreated as previously described, characterized, and tested in the catalytic reactor. Stoichiometry determined by elemental analysis was $\text{NbS}_{1.53}$. Since Alfa was the same company from which the National Bureau of Standards obtained its niobium sulfide, the x-ray pattern, shown in Figure 1, was identical to the one published by NBS as NbS_2 . Analysis by 5-point automated BET gave a surface area of $11.9 \text{ m}^2/\text{g}$.

The second sample was purchased from Strem Chemical Company (catalog no. 93-4115). It was pretreated, characterized, and tested in undoped and doped forms. Elemental analysis revealed a stoichiometry of $\text{NbS}_{1.40}$. Surface area was obtained on a single point manual BET instrument and was $1.37 \text{ m}^2/\text{g}$.

Sample: MK120 File: MK120.SM

Figure 1. X-ray diffraction pattern of NbS_{1.53} obtained from Alfa Chemicals. Three index system (hkl) is used. Thus 1010 is 10.10.

Procedure for Doping NbS_{1.40} with Cs

The NbS_{1.4} catalyst from Strem was doped with Cs at the same unit surface area coverage as the MoS₂. The BET analysis of the NbS_{1.4} indicated a surface area of 1.37 m²/g. This is 35.6 times less than the surface area of the MoS₂. In the dry box, a 1.8 g sample of pretreated NbS_{1.4} was placed in a 200 ml beaker. Next, 18.23 ml of a previously prepared 0.0039 M CsCO₃H in methanol solution was transferred to a 25 ml graduated cylinder. The graduated cylinder was filled to the 25 ml mark with methanol and poured into the beaker containing the NbS_{1.4}. The graduated cylinder was then rinsed with two 10 ml and one 5 ml portion of methanol and poured into the beaker containing the NbS_{1.4}. The methanol was allowed to evaporate under a N₂ flow in the dry box.

Testing Procedure

The reactor was clamped upside down to a ring stand. A glove bag was taped over the end of the reactor and flushed three times with N₂. The glove bag contained the preweighed catalyst, weighing paper, glass wool, the bottom Swagelok fitting, and about 200 ml of clean dry Pyrex beads 3 mm in diameter.

First, approximately 15 cm of beads were poured into the reactor and settled by light tapping with a rubber mallet. Then a disk shaped piece of glass wool was placed in the reactor. This was followed by alternate additions of the catalyst and glass beads to form a uniform catalyst bed 10 cm long in the reactor. Next

another disk of glass wool was placed in the reactor followed by filling the rest of the reactor with beads. A piece of glass wool was inserted into the bottom of the reactor and the bottom Swagelock was fastened. The reactor was then attached to the testing apparatus.

A target gas hourly space velocity (GHSV) of 7750 L/kg catalyst/hr was used for the synthesis gas with a CO/H₂ ratio of unity. The CO flow was measured first until half the target GHSV had been attained to within 1%. A GC injection was made at the time to check that only CO was present in the chromatogram. Next H₂ was added to the CO feed and the flow was adjusted until the target value was attained to less than 1%. The system was pressurized to 81.6 atm. Once at pressure, the CO was first adjusted by stopping the H₂ flow. The H₂ was reintroduced and the total flow adjusted at pressure. The temperature was set to 250°C and sampling begun once every hour. Approximately every 4 hours, the temperature was increased 25°C. Temperatures from 250°C to 350°C were explored. After testing, heaters were turned off, the pressure released, and the catalyst was unloaded under N₂.

Results

Chromatograms were electronically transferred from the integrator to a personnel computer that had the software Chromperfect installed. This program automatically integrates and identifies CO, CO₂, CH₄, H₂O, C₂H₄, C₂H₆, methanol, ethanol, and methyl acetate according to input parameters. When an internal standard is used, Chromperfect can calculate conversions. However, since this work did not use an internal standard, the known number of grams of CO fed into the system per hour allow for a carbon balance to determine CO conversions. All catalytic tests were conducted at 81.6 atm with a CO/H₂ ratio of one.

After characterization of the undoped NbS_{1.55} sample obtained from Alfa, the catalyst was tested using the method described previously. The selectivity and CO conversion are shown in Figures 2 and 3, respectively. Since this test used up the remaining Alfa NbS_{1.53} and the initial catalytic results were low, Cs doping and testing of this catalyst was not attempted.

Figures 4 and 5 show selectivities and yields in g/kg cat/hr for undoped NbS_{1.40} from Strem. Likewise, Figures 6 and 7 show selectivities and yields for the Cs doped NbS_{1.40} catalytic test. Summaries of the activity and selectivity data for all of the NbS_n catalysts, as well as for the MoS₂ and Cs/MoS₂ catalysts,² are given in Tables I and II.

FIGURE 2

Selectivities for NbS1.53 Test

GHSV = 7825 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst.

FIGURE 3

Yields from NbS1.53 Test

GHSV = 7825 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst.

FIGURE 4 Selectivities for NbS1.40 Test

GHSV = 7743 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst.

FIGURE 5

Yields from NbS1.40 Test

GHSV = 7743 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst.

FIGURE 6 **Selectivities for Cs Doped NbS1.40 Test**

GHSV = 7767 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst.

FIGURE 7

Yields from Cs Doped NbS1.40 Test

GHSV = 7767 L/kg cat/hr CO excluded
 Approximate carbon balance does not
 account for carbon formation on catalyst

Table I. Reaction yields (g/kg cat/hr)
at 300°C, 81.6 atm.
GHSV = (7782 ± 38) L/kg cat/hr

	NbS _{1.53}	NbS _{1.40}	Cs doped NbS _{1.40}	MoS ₂ ²	Cs doped MoS ₂ ²
CO ₂	0.453	0	0	235.81	259.59
CH ₄	0.453	0	0	89.11	44.65
H ₂ O	0	0	0	135.69	2.82
C ₂ H ₄	0.453	0	0	24.16	4.31
C ₂ H ₆	0.453	0	0	24.16	4.31
C _n H _{2n+2}	0	0	0	55.41	2.68
MeOH	0.453	0	0	2.75	191.44
EtOH	0	0	0	0	96.34
C3-C4 Alcohol	0	0	0	0	32.13
Esters	0	0	0	0	6.63

Table II. Undoped and doped reaction selectivities
at 300°C, 81.6 atm,
GHSV = (7782 ± 38) L/kg cat/hr

	NbS _{1.53} (%)	NbS _{1.40} (%)	Cs doped NbS _{1.40} (%)	MoS ₂ ² (%)	Cs doped MoS ₂ ² (%)
CO ₂	20	0	0	41.6	40.3
CH ₄	20	0	0	15.7	6.92
H ₂ O	0	0	0	23.9	0.437
C ₂ H ₄	20	0	0	4.26	0.670
C ₂ H ₆	20	0	0	4.26	0.670
C _n H _{2n+2}	0	0	0	9.80	6.40
MeOH	20	0	0	0.485	29.7
EtOH	0	0	0	0	14.9
C3-C4 Alcohol	0	0	0	1.80	4.98
Esters	0	0	0	1.05	1.03

Discussion

Greater success was achieved when $\text{NbS}_{1.84}$ was synthesized from elemental niobium and sulfur. The x-ray pattern matched closely a reference pattern for NbS_2 except that at least three distinct phases are present. It is important to note that the NBS reference x-ray diffraction pattern is from a metal-rich compound in which the stoichiometry has been rounded to NbS_2 . In the metal-rich NbS_2 , additional niobium atoms reside in the octahedral sites between layers. Analysis of a sample by XPS to determine surface stoichiometry by Scofield cross-sectional areas gave a sulfur/niobium ratio of 2.013:1 and a niobium/oxygen ratio of 5.49:1. Thus stoichiometric NbS_2 along with metal-rich phases are probably present. An insufficient amount of sample remained for surface area analysis and catalytic testing. It is possible that a longer annealing period may reduce the presence of unwanted phases.

Catalytic testing of the purchased samples from Alfa and Strem produced selectivities and yields much lower than those reported for Cs doped MoS_2 . Of the two undoped and one doped niobium sulfide test, the undoped sample from Alfa ($\text{NbS}_{1.53}$) had the highest selectivity towards methanol and the highest yield of products. **Figure 2** shows that approximately equal amounts of CH_4 , CO_2 , ethane, ethene, and methanol are produced over the Alfa niobium sulfide at 300°C . Selectivity towards methanol was greatest at 325°C and then dropped off again at 350°C .

Selectivities for the undoped $\text{NbS}_{1.40}$ sample are presented in **Figure 4**. Only two products were detected, CO_2 and CH_4 . Below

350°C, only CO₂ could be detected, even when thermal conductivity detector power was increased 16 times. Most of the conversion occurred at 350°C. Results from the Cs doped NbS_{1.40} test are shown in Figures 6 and 7. Product selectivities are approximately the same as for the undoped test with the exception that water was observed at 350°C.

Overall, the Cs doped NbS_{1.40} sample tested so far is about 20 times less active per unit surface area in terms of CO₂ and CH₄ production than Cs doped MoS₂. Methanol production was observed only in the Alfa NbS_{1.53} sample. A major difference in the niobium sulfide catalysts tested and the MoS₂ catalysts is the surface area. The NbS_{1.53} catalyst may have had greater catalytic activity even in undoped form than the NbS_{1.40} because of a greater surface area (NbS_{1.53} 11.9 m²/g, NbS_{1.40} 1.37 m²/g).

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