CALCULATION OF THE SURFACE AREAS AND THE ACID STRENGTH OF $NiSO_4$, $CuSO_4$ AND $CoSO_4.H_2O$ AND THE USE OF THESE CATALYSTS ON DEHYDRATION OF SOME ALCOHOLS

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$NiSO_4$, $CuSO_4$ ve $CoSO_4.H_2O$'ın Yüzey Alanlarının ve Asidik Kuvvetlerinin Ölçümü ve Bu Katalizörlerin Bazı Alkollerin Dehidrasyon Reaksiyonlarında Kullanılması

ÖZET

Bu çalışmada kullanılan katalizörlerin yüzeyleri elektron mikroskobuyla incelendi ve yüzey alanları gaz adsorpsiyon metoduna göre m^2g^{-1} cinsinden hesaplandı. Ayrıca katı asit katalizörlerde asidik kuvvet ölçümü Hammett indikatör adsorpsiyon metoduna göre tayin edildi. Bu katalizörler ($NiSO_4$, $CuSO_4$, $CoSO_4.H_2O$) kullanılarak, 2,6-dimetil-4-heptanol, 3,7-dimetil-3-oktanol ve 2-oktanol'ün dehidrasyon reaksiyonları incelendi.

Anahtar Kelimeler: Dehidrasyon reaksiyonları, katı asit katalizörler, katı katalizörlerin yüzey asitliği, katı katalizörlerin yüzey alanları, Hammett indikatörleri.

SUMMARY

Calculation of the surface areas and the acid strength of $NiSO_4$, $CuSO_4$ and $CoSO_4.H_2O$ and the use of these catalysts on dehydration of some alcahols

In this study; the surfaces of the catalysts were examined by electron microscope and their surface areas were calculated with gas adsorption method as a unit of m^2g^{-1}. In addition, the acid strength on solid catalysts ($NiSO_4$, $CuSO_4$, $CoSO_4.H_2O$) was determined by Hammett indicator adsorption method and also, dehydration reactions of 2,6-dimethyl-4-heptanol, 3,7-dimethyl-3-octanol and 2-octanol were investigated with the same catalysts

Keywords: **Acidity of catalyst surfaces, solid acid catalysts, Hammett indicators, dehydration reactions.**

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Introduction

Dehydration of alcohols is one of the most familiar reactions to obtain alkenes. Carbonyl compounds and ethers are by-products of the reaction depending on the catalysts used.

Dehydrations can be either homogenous or heterogeneous phases. The metal oxides and anhydrous metal (II) sulphates were used as a catalyst in the heterogeneous dehydration reactions.

Using $NiSO_4$, $CuSO_4$ and $CoSO_4.H_2O$ as heterogeneous catalyst, we investigated the dehydration of alcohols.

Reactions were performed by mixing the alcohol and the catalyst without any solvent and then heated to a temperature 10°C below the boiling temperature of alcohols.
Before and after the reaction, the surface of the catalysts were investigated using the electron microscope and their surface areas were calculated by gas adsorption method[1] as m^2g^{-1}. In addition, the surface acidities of the catalysts were determined by using Hammett indicators[2]. In this experiment, the adsorbed indicator amount on the surface both ammonia poisened and unpoisened catalystwas calculated.

Experimental

Apparatus and Spectrophotometric Procedure: IR spectra run as NaCl discs on a GDU Shidmadzu model 400 spectrophotometer. ^1H NMR spectra were recorded on the Bruce AC 200 MHz spectrometer in $CDCl_3$ with TMS as the interval standard. The UV spectra of the Hammett indicators solutions were taken 200-600 nm wavelength range against reference cyclohexane and benzene in chromatograms were recorded on GC-6AM Shidmadzu apparatus. Electron microscope (Jeol, JSM-T scanning microscope) was used for photographs of the catalysts and screen machine (Retac-3D) for sieving the catalysts.

Reagents: At the dehydration reactions, $CuSO_4.5H_2O$(Merck), $NiSO_4.6H_2O$ (Merck), and $CoSO_4.7H_2O$ (Merck) were used as the catalysts. 2,6-dimethyl-4-heptanol (Aldrich), 3,7-dimethyl-3-octanol (Aldrich) and 2-octanol (Aldrich) were used as alcohols. The other chemicals, the Hammett indicators (Benzalacetophenone, p-dimethylamino azobenzene), cyclohexane, benzene were Merck reagents. They were used directly without further purification.

Procedure

The Preparation of the Catalysts

$CoSO_4.H_2O$ which was prepared by keeping $CoSO_4.7H_2O$ at 220°C for 8 hours was used instead of anhydrous $CoSO_4$. Anhydrous $NiSO_4$ was prepared by leaving $NiSO_4.6H_2O$ for 30 hours at 275°C[3]. And finally, anhydrous $CuSO_4$ was prepared by heating $CuSO_4.5H_2O$ at 275°C for 48 hours (Table I).

Sieving the Catalysts and Investigating at the Electron Microscope

The catalysts were sieved to yield samples with a particle size from 100 to 200 mesh (74-150mm in diameter).

Surfaces of the catalysts (74-150mm particle) were investigated under electron microscope before and after the reaction was run (Figure 1).

Calculating Surface Areas of the Catalysts

Surface areas of the catalysts were calculated from the measurement of N_2 adsorption by applying BET method[1]. According to this method, 0.08-0.1 g catalyst was weighted, placed in a system which was evacuated immediately and then filled with N_2. The amount of N_2 which was adsorbed by the catalyst was measured by a change in the manometer. The volume adsorbed at a given equilibrium was obtained by subtracting from dead volume, determined before, and the last difference was calculated in cm and changed it to a volume, then this operation is repeated by using pressure increase by 50 mm at each time. Surface areas of the catalysts were calculated by BET procedure before and after the reaction was run. For $NiSO_4$, $CuSO_4$ and $CoSO_4.H_2O$, this operation was repeated at the t=20°C and t=90°C.

Table I: Preparation of the catalysts

Catalysts	Heating temperature (°C)	Time (hours)
$CoSO_4.H_2O$	220	8
$NiSO_4$	275	30
$CuSO_4$	275	48

Dehydration Reactions

Alcohol:catalyst (1:1) mixture was used in order to run reactions. The reaction temperatures were kept approximately 10°C lower than boiling point of alcohols in subject. At the end of the reaction, alkenes and water as forming products were collected in a receiver and then extracted with ether. Products were purified by distillation.

Measuring the Acid Strength on the Solid Catalysts

(1)Preparation of the catalysts poisoned with ammonia

The catalysts (74-150mm) were kept under vacuum overnight at 250°C and then were left for 20 hours under 0.5kg/cm^2 pressure of ammonia at the room temperature. To remove physically adsorbed ammonia molecules from the nonacidic surface, we left the catalysts again for 20 hours under the vacuum at room temperature. So that ammonia poisoned catalysts were obtained.

(2) Hammett indicators and solvents

A series of Hammett indicators, their Pka values, the adsorption wavelength to analyse them and nonpolar solvents used in the experiments were listed at the **Table II**.

(3) Adsorption of indicator on the catalysts

Solutions of Hammett indicators were prepared with the solvents listed in Table II and the particles of catalyst which were poisoned with ammonia were put into these solutions. The adsorption equilibrium of indicator on the surface of the catalysts was reached after shaking at the room temperature for 20 hours. The concentration of indicator in solution was estimated by measuring UV absorption at the wavelength listed in Table II. The same operation was repeated with the catalyst particles unpoisoned with ammonia. The amount of indicator adsorbed on the catalyst was calculated from the difference between concentrations of the poisoned and unpoisoned catalysts.

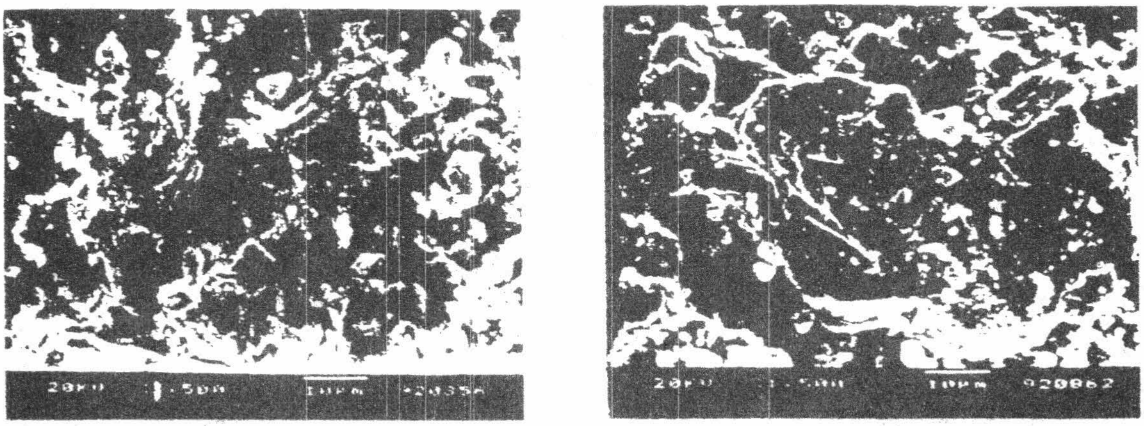
Results and Discussion

Literature procedure 4 was applied to prepare catalysts for dehydration reactions.

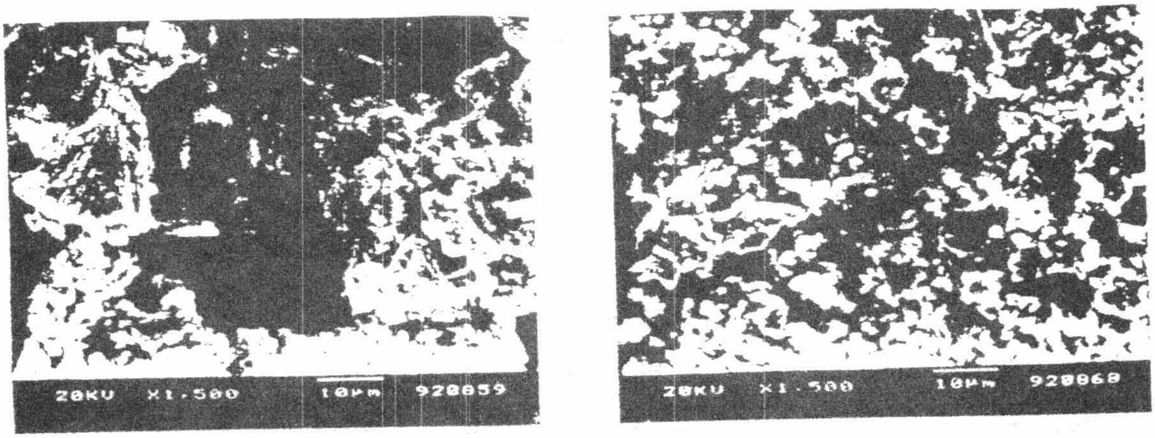
The catalyst crystals which were exposured dehydration reactions were bulkier than catalyst crystals which didn't undergo reactions (Figure1).

Table II: Information related to Hammett indicators used in the experiment.

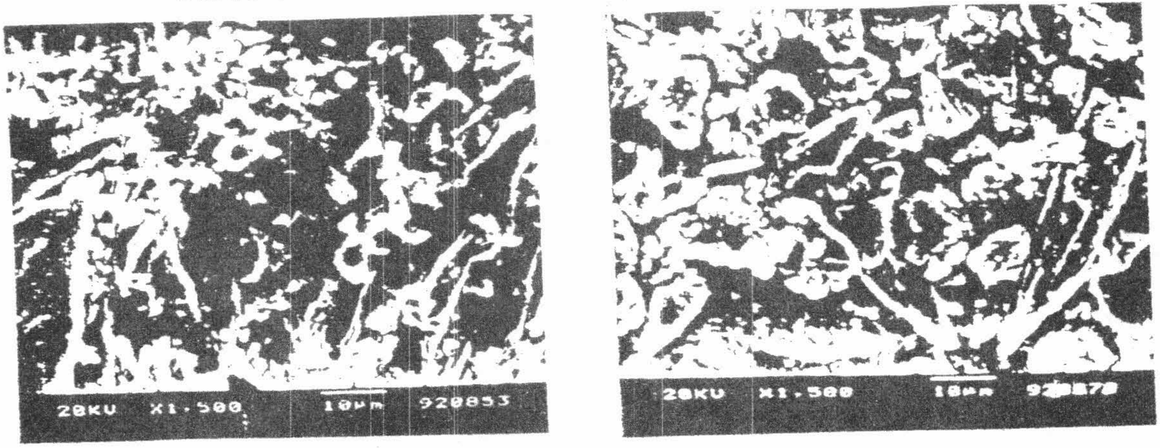
Hammett Indicators	PKa (-)	Nonpolar Solvents	λ_{max}(nm)	Initial concentration (mol/l)
Benzalacetophenone	-5.6	Cyclohexane	295.8	$0.7595.10^{-4}$
p-dimethylamino azobenzene	3.3	Benzene	278.8	$1.5518.10^{-4}$



$NiSO_4$(*) $NiSO_4$



$CuSO_4$(*) $CuSO_4$



$CoSO_4.H_2O$(*) $CoSO_4.H_2O$

Figure 1: Electron microscope photographs of $NiSO_4$, $CuSO_4$ and $CoSO_4.H_2O$ before (*) and after the dehydration reaction

Table III: Calculating the surface areas of the catalysts

T=90°C	The surface area of the catalyst before dehydration react. (m^2g^{-1})	The surface area of the catalyst after dehydration react. (m^2g^{-1})	The lost of the surface area (m^2g^{-1})	% Change
$NiSO_4$	56.0430	45.2478	10.7952	19.26
$CuSO_4$	66.0681	56.8306	9.2372	13.98
$CoSO_4.H_2O$	61.0817	48.4087	12.6730	20.75
T=20°C				
$NiSO_4$	73.8906	56.7674	17.1302	23.18
$CuSO_4$	82.6072	64.7939	17.8133	21.56
$CoSO_4.H_2O$	80.2000	60.4690	19.7310	24.60

The result of calculation of the surface areas by gas adsorption method (BET procedure) of the catalysts were introduced in the Table III.

As shown in the Table III, the order of decreasing surface areas of the catalysts before dehydration reactions is $CuSO_4 > CoSO_4.H_2O > NiSO_4$.

After dehydration reactions, surface areas of the catalysts decreased approximately %20. This case is agreeable with electron microscope pictures. When lower temperatures are used in measurement, the surface areas of the catalysts becomes larger which complies with the theory.

Acidity of the catalyst surface was investigated by Hammett indicators method. The concentration change of the indicator which was measured after treating the ammonia poisoned and unpoisoned catalyst with indicator was used to calculate the acidity (Table IV and Table V).

The Table V showed when p-di methylaminoazobenzene-benzene or benzalacetophenone-cyclohexane solutions were tretead with unpoisoned catalysts, adsorption occured on the catalyst surface judging from the decrease of the concentration of the indicator. When these indicators were treated with the catalysts poisoned with ammonia, we expected no change on the concentration of indicators because of the blockage of acid cites by ammonia. But this was not the case possibly because all the surface could not be poisoned. Consequently, indicator concentration which was chemically adsorbed at the surface was calculated from the difference between indicator adsorption of ammonia poisoned and unpoisoned catalysts. As seen in Table III, when the test occurred with p-dimethylaminoazobenzene-benzene indicator solution, adsorption on the $NiSO_4$ surface was maximum and naturally the surface acidity of $NiSO_4$ was higher than the acidity of $CuSO_4$ and $CoSO_4.H_2O$.

Table IV: The initial concentration of the Hammett indicators

No	Hammett indicators	Nonpolar solvents	λ_{max}(nm)	Initial conc.(mol/l)
1	Benzalacetophenone	Cyclohexane	295.8	$0.7595.10^{-4}$
2	p-dimethylaminoazobenzene	Benzene	278.8	$1.5518.10^{-4}$

Table V: The measuring the results of the acid strength on the catalyst surface

Hammett Indicators	Nonpolar Solvents	Catalysts	The conc. of the Hammett indicators solution (mol/l)	The compare with initial conc. of the Hammett ind. Solutions	Hammett ind. quantity adsorb. on the catalyst surface (mol/l)
Benzal acetophenone	Cyclohexane	$NiSO_4$	$0.5775.10^{-4}$	-	$0.0826.10^{-4}$
	Cyclohexane	$NiSO_4$*	$0.6601.10^{-4}$	-	
	Cyclohexane	$CuSO_4$	$0.7213.10^{-4}$	-	$0.0577.10^{-4}$
	Cyclohexane	$CuSO_4$*	$0.6636.10^{-4}$	-	
	Cyclohexane	$CoSO_4.H_2O$	$0.7028.10^{-4}$	-	$0.0560.10^{-4}$
	Cyclohexane	$CoSO_4.H_2O$*	$0.6468.10^{-4}$	-	
p-dimethyl aminoazo benzene	Benzene	$NiSO_4$	$0.1957.10^{-4}$	-	$1.3642.10^{-4}$
	Benzene	$NiSO_4$*	$1.5599.10^{-4}$	Same	
	Benzene	$CuSO_4$	$1.1305.10^{-4}$	-	$0.5243.10^{-4}$
	Benzene	$CuSO_4$*	$1.6548.10^{-4}$	+	
	Benzene	$CoSO_4.H_2O$	$1.6442.10^{-4}$	+	$0.1182.10^{-4}$
	Benzene	$CoSO_4.H_2O$*	$1.5260.10^{-4}$	-	

*The catalyst was poisoned with ammonia

As a result of dehydration reaction of 2,6-dimethyl-4-heptanol, two important peaks were observed in the gas chromatogram of product mixture. The first one had a retention time 1.14 and peak area %96.4 and the second one had a retention time 1.68 and peak area %3.42. IR spectrum of this product indicated both of the cis structure (726 cm^{-1}) and the trans structure (966 cm^{-1}). The other peaks in the IR spectrum were 1100, 1168, 1363, 1382, 1462, 1641, 2944 cm^{-1}. ^1H NMR spectrum showed of cis and trans structure together at d5.5. Accordingly, these results and structure of this product were determined as a mixture of cis-2,6-dimethyl-3-heptene and trans-2,6-dimethyl-3-heptene.

After dehydration reaction of 3,7-dimethyl-3-octanol, gas chromatogram of obtained product had two peaks. The first one had a retention time 1.41 and peak area %94.8 and the second one had a retention time 2.25 and peak area %3.82. IR spectrum of this product indicated both of the cis (729 cm^{-1}) and the trans (972 cm^{-1}) structure. Other peaks in the IR spectrum 755, 812, 886, 915, 1020, 1068, 1120, 1209, 1369, 1452, 1648, 2944 cm^{-1}. Peak groups were seen d5.7 in the ^1H NMR spectrum. According to the above data, structure of this product was elucidated as a mixed of cis-3,7-dimethyl-3-octene and trans-3,7-dimethyl-2-octene.

IR spectrum of the obtained product after dehydration reaction of 2-octanol showed only trans (963 cm^{-1}) structure. The other peaks 905, 1372, 1452, 1635, 2928 cm^{-1}. ^1H NMR spectrum of obtained product supported to trans-2-octene structure when it was compared with ^1H NMR spectrum of trans-2-octene [5]. All of the evidence above indicated that this product was trans-2-octene.

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