Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis Semi-Annual Report

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Disclaimer:

Patent Information:

No patentable subject matter is disclosed in this report.

Abstract

This report describes the analytical protocols that were developed during the last two years to analyze "spent" THQ (tetrahydroquinoline) slurry liquid. Identification of the components of the "spent" THQ should help to understand the influence of the slurry medium on the methanol synthesis reaction, and on other reactions with THQ as the slurry liquid.

Silica gel liquid chromatography and high performance liquid chromatography (HPLC) were used to isolate and purify the major compounds in the "spent" slurry liquid. Gas chromatography/mass spectroscopy (GC/MS), Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) were applied to identify the major compounds. Methyl -, dimethyl -, and trimethyl - THQ were found to comprise more than 80% of the "spent" liquid. The balance was various methylated indoles. A methyl group always is attached to the N atom in the ring structure. Speculative mechanisms are presented that may help to understand the interaction between the catalyst and the alkylated THQ slurry liquid, and the effect of liquid composition on the methanol synthesis reaction.

A poster entitled "Promoted Zinc Chromite Catalyst for Higher Alcohol Synthesis in a Slurry Reactor – 2. Spent Liquid Analysis" was presented at the AIChE National Meeting, Los Angeles, CA, Nov 12-17, 2000.

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Executive Summary

The effect of slurry liquid composition on the rate and selectivity of methanol synthesis over zinc chromite catalyst was presented in a previous article [1]. It was shown that the rate of methanol synthesis was much higher with tetrahydroquinoline (THQ) as the slurry liquid than with several similar compounds. It also was found that THQ was alkylated during the methanol synthesis reaction. To understand the behavior of the THQ-derived slurry liquid, various analyses were carried out. Silica gel liquid chromatography, high performance liquid chromatography (HPLC) and thin layer chromatography (TLC) were used to isolate the important compounds in the "spent" liquid. Gas chromatography/mass spectroscopy (GC/MS), Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analyses were applied to identify the structure of the compounds. No THQ was found in the "spent" THQ. However, one-methyl, di-methyl, and tri-methyl THQ, with one methyl group always attached to the N atom, were found to constitute more than 80% of the "spent" liquid. Alkylated indoles comprised the remaining 20%. The nitrogen atom always was occupied by one methyl group in both the alkylated THQs, and probably in the alkylated indoles as well. No ethyl groups were detected in the alkylated THQ, which meant that chain growth of methyl group did not occur.

The composition of the liquid in a slurry reactor can have a major influence on the apparent catalyst activity and selectivity. The secondary nitrogen atom in THQ makes this molecule an active nucleophile. This nucleophilicity may help to explain why use of THQ as a slurry liquid enhanced the rate of the methanol synthesis over "zinc chromite" catalyst, and why THQ was transformed rapidly from the pure compound to a complicated mixture of alkylated THQs and indoles.

However, a mechanism to explain how the THQ – derived slurry liquid increases the rate of methanol synthesis still is not clear. The addition of a methyl group to the nitrogen atom greatly reduces the nucleophility. Therefore, the parallel catalytic cycle involving the secondary amine, which was originally postulated [1], appears unlikely.

A poster entitled "Promoted Zinc Chromite Catalyst for Higher Alcohol Synthesis in a Slurry Reactor – 2. Spent Liquid Analysis" was presented at the AIChE National Meeting, Los Angeles, CA, Nov 12-17, 2000.

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A. Introduction

Selection of an appropriate liquid for a slurry reactor is a critical aspect of process feasibility and performance. In a study of methanol synthesis over zinc chromite (Zn/Cr) catalyst in a slurry reactor at temperatures up to 648K, three fused-ring, bicyclic liquids: decahydronaphthalene (DHN), tetrahydronaphthalene (THN) and tetrahydroquinoline (THQ) were examined [1,2]. The composition of the slurry liquid had a pronounced influence on the performance of the catalysts. In particular, the rate of methanol synthesis was much higher with THQ than with the other two liquids.

In that study, the slurry liquid was analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS) during and after the reaction, which involved up to several hundred hours of continuous operation. Decahydronaphthalene and THN underwent little or no reaction. By contrast, THQ was alkylated extensively.

Roberts et al. [1] postulated a link between the alkylation of THQ and the high activity for methanol synthesis that was observed with this compound. However, the simple GC/MS analysis that was carried out in their study was not able to identify the specific alkylated compounds in the slurry liquid. The GC/MS technique had two major deficiencies. First, it could not determine the kind of atom to which the alkyl group was attached, i.e., a carbon atom or a nitrogen atom. Second, the nature of the alkyl groups could not be determined, e.g., whether a compound with two alkyl carbons was a dimethyl or an ethyl compound.

During this report period, we finished developing the analytical protocols that are required to understand the reactions of THQ in the presence of Zn/Cr catalyst under methanol synthesis conditions. This development started in 1998. The report basically is an overview of all the relevant studies that have been carried out on this area. Based on these analyses, we have developed a revised picture of the influence of the THQ – derived slurry liquid on the rate of methanol synthesis.

The value of this research may extend beyond methanol synthesis over zinc chromite. Tetrahydroquinoline has excellent thermal stability under reducing conditions [3] and potentially is useful as a slurry liquid for other reactions (e.g. [4,5]).

B. Results and Discussion

1. Source of "Spent" THQ

The performance of a 'zinc chromite' catalyst previously was studied in a continuous slurry reactor [1] that was operated over a temperature range of 598 to 698 K. The reactor feed was a mixture of hydrogen and carbon monoxide, with a H_2/CO ratio of either 0.5 or 2, and a total pressure of about 14 MPa. Gas hourly space velocity was about 5000 sl/kg-cat/hr.

The zinc chromite catalyst evaluated was a commercial, high-pressure methanol synthesis catalyst (Zn-0312 T1/8) from Engelhard Corporation. "Spent" liquid from the experiment with THQ was obtained by filtering the catalyst slurry

remaining in the reactor after about 240 hours of continuous operation. Details concerning experimental procedure and equipment were given in Roberts et al. [1].

2. Experimental Techniques and Results

2.1. "Spent" THQ Isolation

i. Silica Gel Liquid Chromatography (LC)

In order to obtain samples that contained a small number of compounds, a crude separation was performed using silica gel LC. A detailed description of the silica gel LC operation can be found in References 6-9.

The silica gel LC column was unable to resolve the "spent" THQ into single, pure compounds. Each LC fraction typically contained between 2 and 4 individual compounds. Those fractions that contained essentially the same compounds were combined. This resulted in approximately 20 samples. These samples are referred to as "crude samples". Toluene was chosen as the mobile phase, and was removed from these samples afterwards by evaporation at ambient conditions. All the crude samples were analyzed by gas chromatography/mass spectroscopy (GC/MS) and some of them were analyzed by Fourier transform infrared (FTIR) spectroscopy.

ii. HPLC

In order to remedy the two deficiencies of the previous GC/MS analysis, as noted in the Introduction, it is essential to identify the structure of each major compound in the "spent" THQ. Nuclear Magnetic Resonance (NMR) analysis was required to provide the necessary structural information. However, a fraction containing a single pure compound is required for NMR analysis. High-performance liquid chromatography (HPLC) was used to achieve the further separation of the crude samples into single pure compounds.

Reverse phase HPLC was carried out on a crude sample that contained the three major components of "spent" THQ, based on GC/MS analysis. The HPLC consisted of a Perkin-Elmer liquid chromatography series 200 LC pump with an Adsorbosphere UHS C18 column purchased from Alltech. A Spectroflow 783 UV detector was set at 254 nm. The column had a 30% carbon loading. The column length was 150mm, the diameter was 4.6 mm, and the pore size was 5μm. A sample injection loop of 20μl was used. The mobile phase was 70% acetonitrile and 30% water, and the flow rate was set as 1 ml/min. Multiple injections of the crude fraction were required to obtain sufficient sample for NMR analysis.

2.2. Liquid Fraction Analysis and Results

i. GC/MS Analysis

All the crude samples obtained by the silica gel LC separation were analyzed by GC/MS.

Table 1. Major Components Identified by GC/MS

Formula [a]	MW	Range of LC Fractions # [c]	Mol% [1]	Probable Structure [b]
$C_9H_{11}N$	132	-	0	Tetrahydroquinoline (THQ)
$C_{10}H_{12}$	132	27-35	1.4	Tetrahyronaphthalene
$C_{10}H_{11}N$	145	35-82	3	Dimethyl indoles
$C_{11}H_{13}N$	159	35-82	4	Trimethyl indoles
$C_{12}H_{15}N$	173	35-82	1	Tetramethyl indoles
$C_{10}H_{13}N$	147	84-110	45	Methyl THQ
$C_{11}H_{15}N$	161	84-110	24	Dimethyl/ethyl THQ
$C_{12}H_{17}N$	175	84-110	13	Trimethyl/methyl,ethyl THQ

a. Most probable formula based on GC/MS library
b. Most probable structure based on GC/MS library. Where two compounds are shown, the probabilities were very similar
c. Covered by the crude samples analyzed.

Table 1 shows the major compounds in "spent" THQ based on GC/MS analyses of the crude samples. In agreement with previous GC/MS analyses of an unseparated sample [1], no THQ per se was found in the "spent" THQ. Early LC fractions, covering the range from #27 to #35, contained a small concentration of tetrohydronaphtalene (THN), probably reflecting contamination from a previous experiment.

Three alkylated THQ compounds were found in the late LC fractions covering the range from #84 to #110. The most prevalent was a compound with a molecular weight of 147 and a formula of $C_{10}H_{13}N$. The next most prevalent was a compound with a molecular weight of 161 and a formula of $C_{11}H_{15}N$. The third major compound had a molecular weight of 175 and a formula of $C_{12}H_{17}N$. Previous GC/MS analysis of the whole "spent" THQ [1] showed that these three alkylated THQ's comprised more than 80% of the final liquid.

The crude sample labeled as #103 was comprised of LC fractions #103 to #107. It contained all three of these compounds. Therefore, this sample was further separated into single pure compounds using HPLC for subsequent FTIR and NMR analysis.

Many different alkylated indoles were identified in the crude samples containing the LC fractions from #35 to #82. The presence of these indoles suggests that the saturated ring in THQ had some tendency to open. Crude sample #42, covering the LC fraction range from #42 to #47, contained most kinds of the indoles. Therefore, FTIR analysis was performed on this crude sample to determine whether N-H bonds were present in these alkylated indoles. However, due to the low concentration of each indole, further separation using HPLC was not feasible.

References 6 and 10 describe the GC/MS analysis in more detail.

ii. FTIR Spectroscopy Analysis

Fourier transform infrared analysis was performed on crude fractions #103 and #42 in an attempt to detect the N-H bond in the THQ – derived compounds. The N-H bond has a characteristic peak at about 3450 cm^{-1} in the FTIR spectrum. Therefore, if the FTIR spectra for either sample #103 or #42 had a peak at 3450 cm^{-1}, a N-H bond would be present somewhere in the fraction. The absence of a peak at 3450 cm^{-1} would mean that some functional group other than H occupied the nitrogen atom, or that the N atom was in an aromatic ring.

Figure 1 shows the FTIR spectra of pure THQ and crude sample #103, at approximately equivalent concentrations in chloroform – *d*. Pure THQ has a distinct N-H peak at 3437 cm^{-1}; sample #103 does not. A similar spectrum was obtained for crude sample #42 [6]. Since these two samples contained the alkylated THQ's and the alkylated indoles, we conclude that no N-H bonds are present in these compounds.
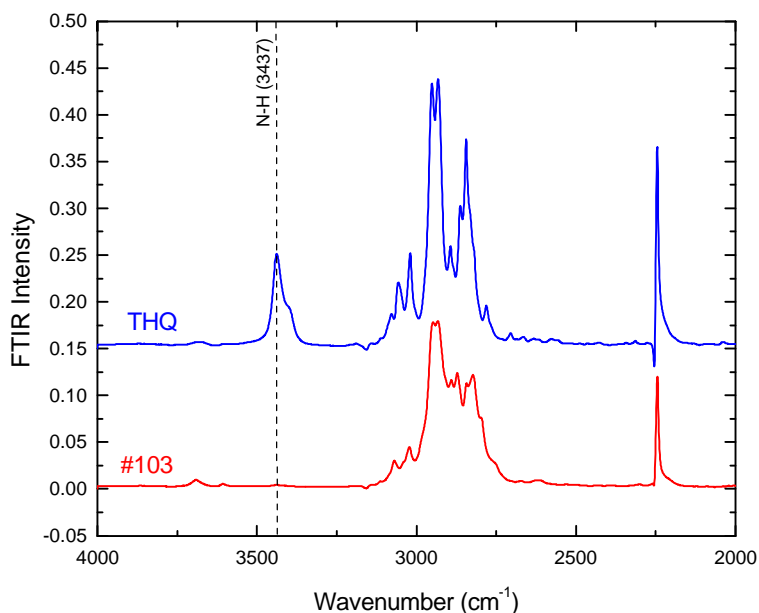

Fig.1   FTIR spectra of pure THQ and Fraction #103. Fraction #103 contains the three compounds that constitute 80% of the "spent" slurry liquid.

iii. HPLC Analysis

Further separation of crude sample #103 was performed using HPLC. The retention times of pure toluene, THQ, and two standard samples: 6-methyl-1, 2, 3, 4-THQ, and 2-methyl-1, 2, 3, 4-THQ also were measured under the same conditions. Table 2 shows a retention time comparison of these compounds. Reverse phase HPLC has a non-polar column and a polar mobile phase. Therefore, more polar compounds tend to elute faster than less polar compounds. Table 2 shows that THQ, 2-methyl THQ and 6-methyl THQ have shorter retention times than toluene due to their stronger polarity, even though toluene has a lower molecular weight.

The three major peaks in sample #103 had retention times of 8.32 min, 12.51 min, and 18.30 min, much longer than either 2 - or 6 - methyl THQ and toluene. Based on this, we conclude that the nitrogen atom in these alkylated THQ compounds is occupied by an alkyl group, which would greatly reduce the polarity of the compounds and increase the retention time. The conclusion that the N atom in the THQ-derived compounds is occupied by an alkyl group is consistent with the FTIR results presented above.

Table 2. HPLC Retention Time Comparison

Structure				
Rt (min)[a]	4.13	5.49	5.57	6.05
Compound	$C_{10}H_{13}N$	$C_{11}H_{15}N$	$C_{12}H_{17}N$	
Structure				
Rt (min)[a]	8.32	12.51	18.30	

a.   Rt denotes retention time.

iv. NMR Analysis

Nuclear magnetic resonance measurements were performed on the three pure compounds obtained after HPLC separation. These three compounds constituted more than 80% of the "spent" THQ based on the previous GC/MS analysis of the total "spent" THQ sample.

Identification of the important structural groups in the THQ – derived compounds was done by comparison of the acquired NMR spectra with the spectra of pure compounds with similar structural groups.

Proton NMR spectra are available for four compounds that are similar to those in the THQ-derived slurry liquid: 3-methyl-5, 6, 7, 8-THQ, 6-methyl-1, 2, 3, 4-THQ, 2-methyl-1, 2, 3, 4-THQ (tetrahydroquinodine) and 2-methylene-1, 3, 3-trimethylindoline [11]. These standard spectra provided the chemical shift for protons in positions of interest [6].

Figure 2 shows the proton NMR spectra of the compound $C_{10}H_{13}N$, the compound $C_{11}H_{15}N$, and the compound $C_{12}H_{17}N$, as obtained from crude sample #103 using HPLC. In the NMR spectrum of the fraction containing $C_{10}H_{13}N$, a sharp singlet peak shows at a position close to 3.0 ppm, and aromatic proton signals show between 6.5 and 7.5 ppm. In conjunction with the GC/MS and FTIR results, we conclude that this compound ($C_{10}H_{13}N$) is 1-methyl THQ. The methyl group is attached on the nitrogen atom. The absence of a signal between 7.5 and 8.5 ppm suggests that there are no N-containing aromatic rings in this compound.
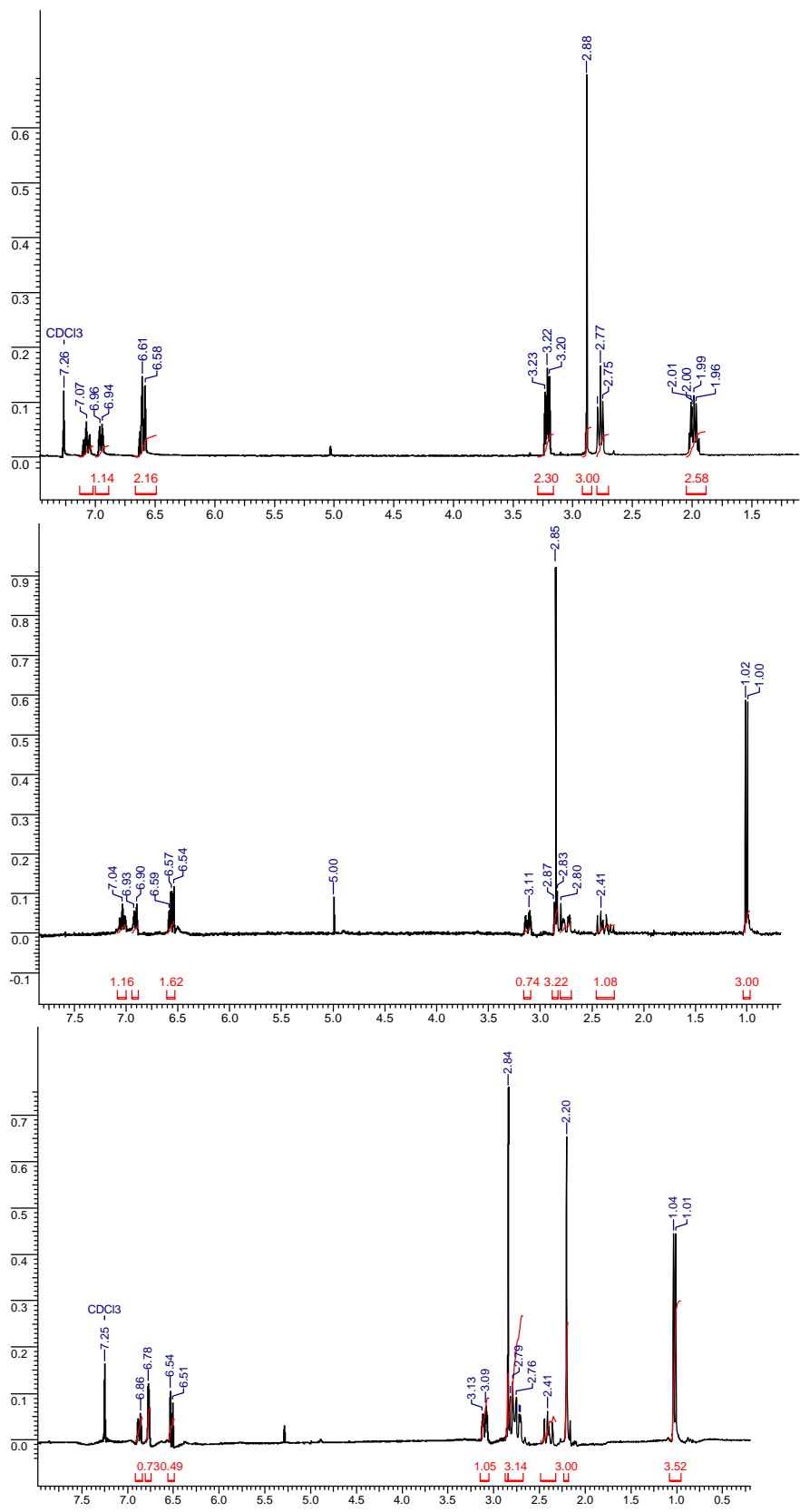
Fig.2   NMR spectra for compounds: a) $C_{10}H_{13}N$, b) $C_{11}H_{15}N$, and c) $C_{12}H_{17}N$.
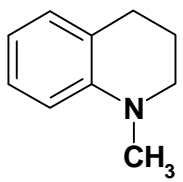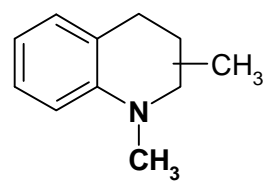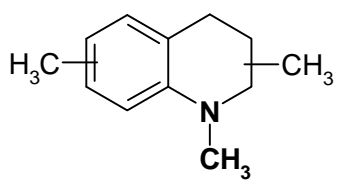
In the spectrum of the fraction containing $C_{11}H_{15}N$, a singlet peak shows at a position close to 3.0 ppm, and a doublet shows at a position close to 1.3 ppm. Two methyl groups may contribute to these two peaks. One is a methyl group attached on the nitrogen atom, while the other one is a methyl group attached to a carbon in the saturated ring. For an ethyl group ($-CH_2CH_3$), the upfield CH_3 signal would be split into a three-line multiplet (a triplet) because of the coupling of the adjacent methylene - CH_2 -group, while the methylene (CH_2) signal would be split into a five-line multiplet because of the coupling of the adjacent methyl group and the coupling with the single hydrogen on the other side of the methylene group. There is no evidence of such splitting in Fig.2. Therefore, based on this NMR spectrum and on the GC/MS and FTIR results, this THQ with two alkyl carbons appears to be dimethyl THQ, rather than ethyl THQ, with one methyl group attached to the N atom and the other one attached to a carbon in the saturated ring.

In the NMR spectrum of the fraction containing $C_{12}H_{17}N$, two sharp singlet peaks show at positions close to 3.0 ppm and 2.2 ppm. Also, a doublet signal shows at about 1.3 ppm. This three-alkyl-carbon THQ appears to be trimethyl THQ. One methyl group is attached on the nitrogen atom. The second methyl group is on the saturated ring, and the third is on the aromatic ring.

A peak at 7.26 ppm, characteristic of deuterated chloroform, is common to all three spectra.

Table 3 shows the identified structures of compounds $C_{10}H_{13}N$, $C_{11}H_{15}N$ and $C_{12}H_{17}N$. These three compounds constitute more than 80% of the "spent" THQ. Due to the complexity of the NMR spectra, we have not attempted to define the exact position(s) of all the methyl group(s) on the THQ molecule.

Table 3. Structures of the Compounds $C_{10}H_{13}N$, $C_{11}H_{15}N$, and $C_{12}H_{17}N$

$C_{10}H_{13}N$	$C_{11}H_{15}N$	$C_{12}H_{17}N$

3. Discussion

Methanol synthesis is believed to involve the hydrogenation of formyl intermediates on the catalyst surface, which are formed by CO insertion into a metal hydride, as shown in Fig.3 (Route I) [12-14]. Tetrahydroquinoline, with a lone pair of electrons on the nitrogen atom, is an active nucleophile. The nitrogen atom in THQ can attack the carbonyl group in the formyls on the catalyst surface to form a hemiaminal. Hydrogenolysis of the C-N bond in the hemiaminal leads to methanol and regenerates THQ. In a previous paper,

Roberts et al. [1] suggested this series of reactions as an explanation for the enhanced rate of methanol synthesis in THQ, relative to the other two liquids, DHN and THN. The route proposed showed THQ participating in a parallel catalytic cycle, with the secondary amine being regenerated as shown in Fig. 4 (Route II). To explain how this parallel catalytic cycle could operate in the absence of THQ per se, the authors [1] speculated that some of the alkyl-THQ might be secondary amines, with alkyl groups on C atoms rather than on the N atom.

The present analytical results do not support this hypothesis. It is clear that an alkyl group always is attached to the N atom in the "spent" THQ liquid. Tertiary amines are much less reactive than secondary amines, and the hypothesis of a rapid parallel cycle is much less plausible.

The hemiaminal intermediate in Route II also might undergo a second hydrogenolysis reaction, hydrogenolysis of the C-O bond, as shown in Fig.5 (Route III). This results in methyl THQ plus water. Although this reaction provides a pathway to the 1-methyl THQ that was observed in the present analyses, it does not explain the enhanced rate of CH_3OH formation that was observed. In fact, the nucleophilic addition plus the hydrogenolysis of Route III could even act to slow down the overall rate of methanol synthesis since it competes with direct hydrogenation of formyl intermediates to form methanol.

Here, we propose another scheme to explain the enhanced rate of methanol synthesis with THQ, which involves the THQ trapping effect [15-18].

A side effect of methanol synthesis by hydrogenation of adsorbed formyl intermediates on the catalyst surface (Fig. 3) would be hydrogenation and dehydration, which would generate water and an adsorbed methyl group
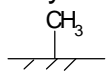
, as shown in Fig.6 (Route IV). At best, surface methyls would act as a "dead" intermediate, occupying active sites on the catalyst surface and retarding to the overall methanol synthesis rate. The present analytical results show that one THQ molecule can trap up to three methyl groups within 240 operating hours, which suggests that THQ is a very efficient trapping reagent. Using THQ as the slurry medium might lead to "scavenging" of the surface methyl groups, leaving more catalyst surface. This might be responsible for the observed increased rate of methanol formation.
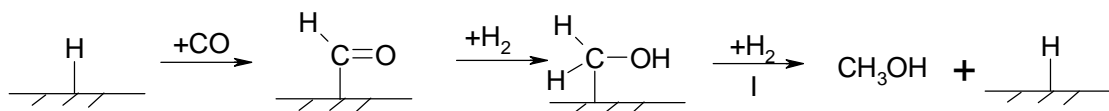

Fig.3   Methanol synthesis on the catalyst surface – hydrogenation of formyl intermediate. (Route I)
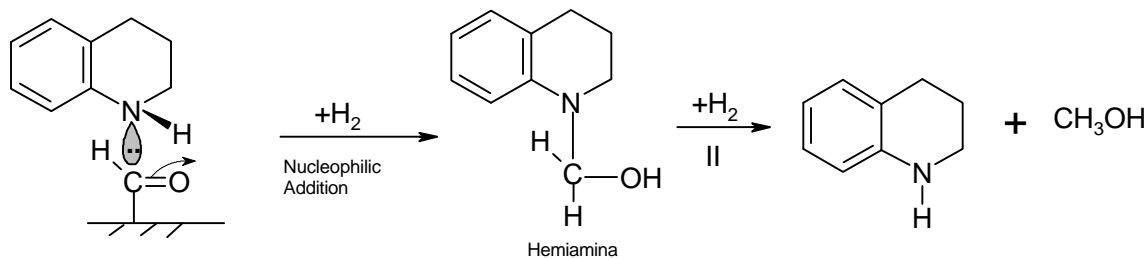
Fig.4   THQ nucleophilic addition to formyl intermediate to form methanol and regenerate THQ. (Route II)
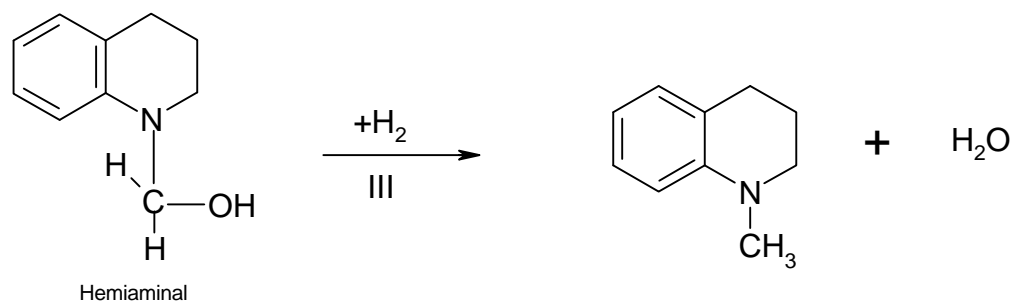

Fig.5   THQ nucleophilic addition to formyl intermediate to form alkyl THQ. (Route III)
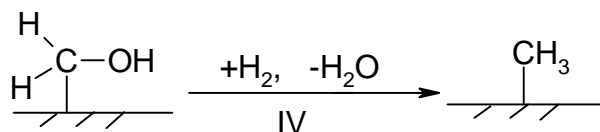

Fig.6   Side reaction of methanol synthesis – dehydration of formyl intermediate - methyl intermediate formation. (Route IV)

4. Technical Presentation

A poster entitled "Promoted Zinc Chromite Catalyst for Higher Alcohol Synthesis in a Slurry Reactor – 2. Spent Liquid Analysis" was presented at the AIChE National Meeting, Los Angeles, CA, Nov 12-17, 2000. The poster explained the motive of this research, described the analytical protocols that were developed to analyze the "spent" THQ (tetrahydroquinoline) slurry liquid and showed all the results obtained.

C. Conclusions

The composition of the liquid in a slurry reactor can have a major influence on the apparent catalyst activity and selectivity. The secondary nitrogen atom in THQ makes this molecule an active nucleophile. This nucleophilicity may help to explain why use of THQ as a slurry liquid enhanced the rate of the methanol synthesis over "zinc chromite" catalyst, and why THQ was transformed rapidly from the pure compound to a complicated mixture of alkylated THQs and indoles. Using a variety of analytical techniques, it has been shown that pure THQ was

alkylated to methyl, dimethyl and trimethyl THQ, and that these three compounds constituted about 80% of the final slurry liquid. Alkylated indoles comprised the remaining 20%. The nitrogen atom always was occupied by one methyl group in both the alkylated THQs, and probably in the alkylated indoles as well. No ethyl groups were detected in the alkylated THQ, which meant that chain growth of methyl group did not occur.

The reason why the THQ – derived slurry liquid is able to increase the rate of methanol synthesis still is not clear. The addition of a methyl group to the nitrogen atom greatly reduces the nucleophility. Therefore, the parallel catalytic cycle involving the secondary amine that was originally postulated [1] appears unlikely.

D. References

1. G.W. Roberts, M.A. Marquez, C.A. Haney, Applied Catalysis A: General 183 (1999) 395-410.
2. M.A. Marquez, The Stability of Liquids and the Effect of their Composition on the Production of Methanol in a Slurry Reactor, M.S. Thesis, North Carolina State University (1996).
3. G.W. Roberts, M.A. Marquez, M.S. McCutchen, C.A. Haney, I.D. Shin, Ind. Eng. Chem. Res. 36 (1997) 4143.
4. E.H. Schreiber, M.D. Rhodes, G.W. Roberts, Applied Catalysis B: Environmental 23 (1999) 9-24.
5. E.H. Shreiber and G.W. Roberts, Applied Catalysts B. Environmental, 26 (2000) 119-129.
6. X. Sun, N. W. Jones, J. C. Gesick, L. Xu, G. W. Roberts, "Liquid/Catalyst Interactions in Slurry Reactor: Changes in Tetrahydroquinoline Composition over Zinc Chromite during Methanol Synthesis", submitted to Applied Catalysis A. General.
7. X. Sun, G. W. Roberts, Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis: Semi-Annual Report (Period Ending 3/31/98).
8. X. Sun, G. W. Roberts, Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis: Semi-Annual Report (Period Ending 9/30/98).
9. X. Sun, G. W. Roberts, Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis: Semi-Annual Report (Period Ending 9/30/99).
10. X. Sun, G. W. Roberts, Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis: Semi-Annual Report (Period Ending 3/31/00).
11. Integrated Spectral Data Base for Organic Compounds, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan. (http://www.aist.go.jp/R10DB/SDBS/menu-e.html)
12. J. Saussey, J.C. Lavalley, J. Lamotte, T. Rais, Spectroscopic evidence of formyl species formed by CO and H_2 co-adsorption on ZnO and Cu-ZnO, J. Chem. Soc. Chem. Commun. 5 (1982) 278.
13. A. Deluzarche, J.P. Hindermann, R. Kieffer, Caron monoxide-hydrogen reactions: possible reaction mechanisms in heterogeneous catalysis, J. Chem. Res. (Synopses) 3 (1981) 72.

14. S. Lee, Methanol Synthesis Technology, CRC Press, Florida, (1990) 227.
15. G.A. Kliger, O.A. Lesik, A.I. Mikaya, E.V. Marchevskaya, V.G. Zaikin, L.S. Glebov, S.M. Loktev, Izv. Akad. Nauk. SSSR, Ser. Khim. 503 (1991) 435.
16. G.A. Kliger, L.S. Glegov, T.P. Popova, E.V. Marchevskaya, V.G.Beryezkin, S.M. Loktev, J. Catal. 111 (1988) 418.
17. G.A. Kliger, L.S. Glebov, R.A. Fridman, E.I. Bogolepova and A.N. Bashkiron, Kinet. Catal. 19 (1978) 619
18. L.S. Glegov, G.A. Kliger, T.P. Popova, V.E. Shiryaeva, V.P. Pyzhikov, E.V. Marchevskaya, O.A. Lesik, S.M. Loktev, V.G. Beryezkin, J. Molec. Cata. 35 (1986) 335