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HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

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EXECUTIVE SUMMARY

The objective of the research was to develop the methodology for the catalytic synthesis of ethers, primarily methyl isobutyl ether (MIBE) and methyl tertiary butyl ether (MTBE), directly from alcohol mixtures that are rich in methanol and 2-methyl-1-propanol (isobutanol). The overall scheme involves gasification of coal, purification and shifting of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers. The last stage of the synthesis involves direct coupling of synthesis gas-derived methanol and isobutanol that has been previously demonstrated by us to occur over superacid catalysts to yield MIBE and smaller amounts of MTBE at moderate pressures and a mixture of methanol and isobutene at low pressures.

The effectiveness of solid acid catalysts for the conversion of methanol and isobutanol mixtures to ethers or precursors to ethers was investigated. The target ethers are those which possess beneficial fuel additive characteristics such as high octane or high cetane values for use in gasoline or diesel fuels, respectively. In addition, these ethers possess environmentally beneficial properties in that they are oxygenates and their use in automotive fuels reduces carbon monoxide emissions. Indeed, the use of oxygenated fuels is required in many major metropolitan areas during winter months.

Several very selective novel reactions have been discovered over the course of this work. H-Mordenite can selectively convert, at relatively low temperatures, i.e. 90-150°C, the methanol in the methanol/isobutanol mixture to dimethyl ether (DME) while leaving the isobutanol unconverted. Acidic ion-exchange resins, particularly Nafion-H, have been shown to directly couple the two alcohols to MIBE selectively at 90°C.

Sulfate-modified zirconia converts isobutanol selectively, in high yield, in the presence

of an equimolar amount of methanol, to isobutene with minimal conversion of methanol. This essentially converts the methanol/isobutanol mixture to a methanol/isobutene mixture that is the direct feedstock in the current commercial process for MTBE production. This highly selective and novel reaction is the critical step in the efficient production of MTBE from C_1 sources such as coal, natural gas, and biomass.

The direct conversion of methanol and isobutanol to MTBE, although thermodynamically viable, has been found to be kinetically unfavored over other acid catalyzed reactions. The conversion, however, may be realized in a 2-step process utilizing the high selectivity of sulfate-modified zirconia catalyst for the initial dehydration of isobutanol to isobutene. Then the methanol/isobutene mixture can be converted, at lower temperature over Amberlyst-15, to MTBE. Because the initial isobutanol dehydration occurs in the presence of methanol, the need for a costly alcohol separation step following higher alcohol synthesis is eliminated.

The sulfate-modified zirconia was characterized extensively. The treatment of the zirconia precursor with sulfate was found to be crucial as the sulfate-free zirconia was found to be totally inactive for the methanol-isobutanol reactions even at elevated temperatures. The addition of sulfate was also found to stabilize the high surface area of the catalyst. X-ray photoelectron spectroscopy (XPS) of pyridine adsorbed on ZrO_2/SO_4^{2-} shows the presence of both Bronsted and Lewis type acid centers. Aqueous titration of water-treated sulfated zirconia revealed that all of the sulfate groups can be converted to mono-protic surface Brönsted acid.

TABLE OF CONTENTS

	Page No.
Title Page	1
Disclaimer	2
EXECUTIVE SUMMARY	3
TABLE OF CONTENTS	5
LIST OF FIGURES	7
LIST OF TABLES	12
I. Background of C_5 Ether Synthesis	14
A. Selection of the Organic Resin Catalysts	16
B. Experimental Testing of the Catalysts	17
II. MTBE Synthesis From Methanol and Isobutene Over Resin Catalysts	20
A. Comparison of Acidic Ion-Exchange Resin Catalysts	20
B. Temperature Dependence of MTBE Synthesis Over Purolite	22
C. Space Velocity Dependence Over Purolite	23
III. Ether Synthesis From Methanol and Isobutanol Over Resin Catalysts	25
A. Ether Synthesis via Coupling of Methanol and Isobutanol	25
B. High Temperature Testing of Nafion-H MS, and Nafion-K	30
C. Nafion-H MS Activity Dependence on Sodium Content	31
D. Characterization of Newer Amberlyst Catalysts	33
E. Mechanism of MIBE Formation Over Nafion-H: Isotope Labelling Study of Ether Synthesis Over Nafion-H	51
IV. Inorganic Catalysts for Direct Coupling of Alcohols to Ethers	58
A. Standard Test Screening of Inorganic-Based Catalysts	58
B. Effect of Water on the Reaction Rate Over γ-Alumina	68
C. Dehydration of Alcohols Over Silica and Zirconia Supported PW_{12} Heteropolyacid, Nb_2O_5, and $Fe/Mn/ZrO_2/SO_4^{2-}$ Catalysts	72
D. Dehydration of Isobutanol Over H-Mordenite	89
E. X-Ray Powder Diffraction of H-Mordenite and H-ZSM-5 Zeolites	90
F. Scanning Electron Microscopy of H-Mordenite and HZSM-5 Zeolite	95
G. Molecular Modelling of Alcohol Reactions in H-Mordenite	101

V. Extended Reactivity Studies Over the ZrO_2/SO_4^{2-} Catalyst 107

A. Alcohol Pressure Dependence on Product Selectivity 107
B. Reaction of Methanol/Isobutanol Mixture over ZrO_2/SO_4^{2-} 110
C. Effect of Isobutanol Pressure on Mixed Alcohol Dehydration 115
D. Pressure Dependence on Methanol Dehydration 115
E. Pressure Dependence of Isobutanol Dehydration 117
F. Dehydration of Isobutanol Only Over ZrO_2/SO_4^{2-} 117
G. Dehydration of Primary Alcohols Over the ZrO_2/SO_4^{2-} Catalyst 124
H. The Effect of Water on Reaction of MeOH/i-BuOH Over ZrO_2/SO_4^{2-} 124

VI. Characterization of the ZrO_2/SO_4^{2-} Catalyst 129

A. Surface Area of the ZrO_2/SO_4^{2-} Catalyst 129
B. Calculation of Amount of Sulfur on Sulfated Zirconia 131
C. Determination of Acidity *via* Aqueous Titration of ZrO_2/SO_4^{2-} 133
D. Catalyst Characterization using X-Ray Photoelectron Spectroscopy (XPS) 137
E. Probing the Acidity of Sulfate-Modified Zirconia by XPS 141
F. Quantification of XPS Data: Amount of Sulfur on Sulfate-Modified Zirconia 146

VII. Octane and Cetane Number Determination 149

A. Octane Number Determination 149
B. Cetane Number Determination 150

VIII. Experimental Methods 151

A. Calibration of Thermal Response Factors and GC Parameters 151
B. Gas Chromatographic Analysis with Mass Spectrometric Detection 153
C. ^1H NMR to Resolve Whether 1-Butene was a Product 154
D. Liquid Phase Alcohol Coupling Reactions 155

IX. Conclusions 160

X. Acknowledgements 163

XI. References 164

LIST OF FIGURES

Page No.

Figure 1. Schematic of the reaction system. 18

Figure 2. The present commercial process for the production of MTBE. 21

Figure 3. The product selectivities of the organic resin catalysts at 90°C and 1 atm with methanol/isobutanol = 1/1 reactants. 29

Figure 4. The product ratios of MTBE/isobutene, MIBE/DME, and MIBE/MTBE over the organic resin catalysts at 90°C and 1 atm with methanol/isobutanol = 1/1 reactants. 29

Figure 5. Schematic of Amberlyst structure. 34

Figure 6. Selectivity for Amberlyst 1010 in mole % of products. 40

Figure 7. Selectivity for Amberlyst 35 in mole % of products. 41

Figure 8. Selectivity for Amberlyst 36 in mole % of products. 42

Figure 9. % Yield for Amberlyst 1010 based on methanol conversion. 43

Figure 10. % Yield for Amberlyst 35 based on methanol conversion. 44

Figure 11. % Yield for Amberlyst 36 based on methanol conversion. 45

Figure 12. % Yield for Amberlyst 1010 based on isobutanol conversion. 46

Figure 13. % Yield for Amberlyst 35 based on isobutanol conversion. 47

Figure 14. % Yield for Amberlyst 36 based on isobutanol conversion. 48

Figure 15. Space time yields of the ethers and butenes formed over Amberlyst-35 as a function of the alcohol partial pressure at 90°C. 50

Figure 16. Space time yields of the ethers and butenes formed over Amberlyst-35 as a Function of the Alcohol Partial Pressure at 117°C. 50

Figure 17. Isotopic composition of the reaction of methanol-^{18}O and isobutanol-^{16}O over Nafion-H at 90°C. 54

Figure 18. The reaction pathway for O^{18}-methanol and O^{16}-isobutanol to form O^{16}-MIBE. 56

Figure 19. The mechanism for isobutanol dehydration to form isobutene, with subsequent reaction of O^{18}-methanol to form O^{18}-MTBE. 57

Figure 20. Conversion of methanol over four acidic inorganic catalysts under the reaction conditions given in Table 15. 62

Figure 21. Conversion of isobutanol over four acidic inorganic catalysts under the reaction conditions given in Table 15. 62

Figure 22. The product selectivity over H-mordenite from methanol/isobutanol = 1/1 reactant at 0.1MPa as a function of temperature. 63

Figure 23. The product selectivity over the sulfated zirconia catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 64

Figure 24. The product selectivity over montmorillonite from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 65

Figure 25. The product selectivity over the silica-alumina catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 65

Figure 26. The product yields over the H-ZSM-5 zeolite catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 67

Figure 27. The product yields over the γ-alumina catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 67

Figure 28. The effect of the methanol/isobutanol = 1/1 reactant being dry or wet on the productivities of the γ-alumina catalyst. 70

Figure 29. Space time yields of products over PW_{12}/SiO_2 catalyst calcined at 100°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 75

Figure 30. Space time yields of products over PW_{12}/SiO_2 catalyst calcined at 200°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 76

Figure 31. Space time yields of products over PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 78

Figure 32. Percent yields of products (based on reactant conversion) over PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 79

Figure 33. Percent yields of products over PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 80

Figure 34. Space time yields of products over $Nb_2O_5 \cdot nH_2O$ catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 82

Figure 35. Percent yields of products (based on reactant conversion) over $Nb_2O_5 \cdot nH_2O$ catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 83

Figure 36. Space time yields of products over $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst calcined at 620°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 84

Figure 37. Percent yields of products (based on reactant conversion) over $Fe/Mn/ZrO_2/SO_4^{2-}$catalyst calcined at 620°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 85

Figure 38. Percent yields of products (based on reactant conversion) over $Fe/Mn/ZrO_2/SO_4^{2-}$catalyst calcined at 720°C from methanol /isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 87

Figure 39. Space time yields of products over $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst calcined at 720°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature. 88

Figure 40. The dehydration behavior of isobutanol only over the H-mordenite catalyst as a function of reaction temperature. 91

Figure 41. XRD pattern of H-mordenite prior to catalytic testing. 93

Figure 42. XRD pattern of H-mordenite after catalytic testing. 94

Figure 43. XRD pattern of H-ZSM-5 zeolite prior to catalytic testing. 96

Figure 44. XRD pattern of H-ZSM-5 zeolite after catalytic testing. 97

Figure 45a.Scanning electron micrograph of H-mordenite prior to catalytic testing. The magnification is 1,000 X and 10 mm equals 10 μm. 99

Figure 45b.Scanning electron micrograph of H-mordenite after catalytic testing. The magnification is 1,000 X and 10 mm equals 10 μm. 99

Figure 46a.Scanning electron micrograph of H-ZSM-5 zeolite prior to catalytic testing. The magnification is 1,000 X and 10 mm equals 10 μm. 100

Figure 46b. Scanning electron micrograph of H-ZSM-5 zeolite after catalytic testing. The magnification is 1,000 X and 10 mm equals 10 μm. 100

Figure 47a. Visualization of a methanol molecule in the main channel reacting with methoxonium ion in the side-pocket of H-Mordenite. 106

Figure 47b. Visualization of an isobutanol molecule in the main channel reacting with methoxonium ion in the side-pocket of H-Mordenite, notice size limitions of this orientation. 106

Figure 48. Effect of alcohol partial pressure on product yields for the reaction of methanol/isobutanol = 1/1 over ZrO_2/SO_4^{2-} catalyst at 116°C. 108

Figure 49. Effect of alcohol partial pressure on product yields for the reaction of methanol/isobutanol = 1/1 over ZrO_2/SO_4^{2-} catalyst at 157°C. 109

Figure 50. Equilibrium distribution of butene isomers. 111

Figure 51. Contact time dependence of reaction of methanol/isobutanol = 2/1 over ZrO_2/SO_4^{2-} catalyst at 157°C. 113

Figure 52. Butene product selectivity of reaction of methanol/isobutanol = 2/1 over ZrO_2/SO_4^{2-} catalyst at 157°C. 114

Figure 53. Space time yields of products as a function of isobutanol pressure over ZrO_2/SO_4^{2-} catalyst at 157°C, 0.1 MPa total pressure. 116

Figure 54. Space time yields of products as a function of methanol pressure over ZrO_2/SO_4^{2-} catalyst at 157°C, in the absence of isobutanol. 118

Figure 55. Space time yields of products as a function of isobutanol pressure over ZrO_2/SO_4^{2-} catalyst at 157°C, 0.1-3.0 MPa total pressure, in the absence of methanol. 119

Figure 56a. Space time yields of products for the dehydration of isobutanol only over ZrO_2/SO_4^{2-} catalyst as a function of temperature. 121

Figure 56b. Space time yields of products for the dehydration of isobutanol only over ZrO_2/SO_4^{2-} catalyst as a function of space velocity at 200°C. 122

Figure 56c. Space time yields of products for the dehydration of isobutanol only over ZrO_2/SO_4^{2-} catalyst at 200°C, isobutanol feed = 20.69 mol$*$(kg cat)$^{-1}*$hr^{-1}. 123

Figure 57. Conversion of primary alcohols over ZrO_2/SO_4^{2-} catalyst at 157°C, alcohol feed = 1.72 mol$*$(kg cat)$^{-1}*$hr^{-1}. 125

Figure 58. Effect of water feed on reaction of methanol/isobutanol = 2/1 over ZrO_2/SO_4^{2-} catalyst at 157°C, 0.1 MPa total pressure. 127

Figure 59. XPS of oxygen 1s region of ZrO_2/SO_4^{2-} catalyst. 135

Figure 60. XPS of sulfur 2p region of ZrO_2/SO_4^{2-} catalyst. 136

Figure 61. XPS of zirconium 3d region of ZrO_2/SO_4^{2-} catalyst. 138

Figure 62. Schematic of new high vacuum system for pretreatment of XPS samples. 140

Figure 63. XPS of N 1s region of dry ZrO_2/SO_4^{2-} catalyst adsorbed with pyridine. 142

Figure 64. XPS of N 1s region of wet ZrO_2/SO_4^{2-} catalyst adsorbed with pyridine. 143

Figure 65. XPS of N 1s region of γ-alumina catalyst adsorbed with pyridine. 145

Figure 66. XPS of N 1s region of Nafion-H catalyst adsorbed with pyridine. 147

Figure 67. NMR Spectrum of pure isobutene in $CDCl_3$. 156

Figure 68. NMR Spectrum of pure 1-butene in $CDCl_3$. 157

Figure 69. NMR Spectrum of isobutanol dehydration products in $CDCl_3$. 158

LIST OF TABLES

Page No.

Table 1. MTBE synthesis *via* methanol and isobutene coupling at 75°C and 0.1 MPa. Total flow rates for the three tests were the following: Purolite C-150 = 1950 mol/kg/hr, BioRad = 1975 mol/kg/hr, and Amberlyst-15 = 2015 mol/kg/hr. 22

Table 2. Results of methanol and isobutene coupling over Purolite C-150 as a function of temperature at 0.1 MPa (catalyst weight = 0.26 g). 23

Table 3. Results of methanol and isobutene coupling to form MTBE over Purolite C-150 as a function of reactant space velocity at 0.1 MPa and 75°C (catalyst weight = 0.25 g). 24

Table 4. Activities of the resin catalysts in the MeOH + i-BuOH standard test. 27

Table 5. Activities of the Nafion-H MS catalyst in the MeOH + i-BuOH standard test as a function of temperature. 30

Table 6. Yield of non-exchanged and 18% exchanged Nafion-H MS. 32

Table 7. Surface areas of the Amberlyst resins. 35

Table 8. % Swelling of Amberlyst resins in water and methanol. 36

Table 9. Ion exchange titration data for Amberlyst -1010, -35, and -36 resins. 36

Table 10. Amberlyst-1010 activity as a function of temperature. 37

Table 11. Amberlyst-35 activity as a function of temperature. 38

Table 12. Amberlyst-36 activity as a function of temperature. 38

Table 13. Activity of polymeric resin catalysts at 90°C. 39

Table 14. Space time yields of products formed by the reaction of ^{18}O-methanol and ^{16}O-isobutanol over Nafion-H at 90°C and 101 kPa. 53

Table 15. Product yields (mol/kg cat/hr) over inorganic catalysts at 1 atm as a function of temperature. Reactant feed was methanol = 1.72 mol/kg cat/hr, isobutanol = 1.72 mol/kg cat/hr. 61

Table 16. Surface areas. 89

Table 17. Space time yields of the products (mol/kg cat/hr) formed over H-mordenite and H-ZSM-5 zeolite from methanol = isobutanol = 1.72 mol/kg cat/hr reactants in He/N_2 carrier gas at 0.1 MPa as a function of temperature. 101

Table 18. Surface areas determined by nitrogen absorption/desorption. 130

Table 19. Surface area of the sulfated zirconia *vs* calcination temperature. 130

Table 20. Result of elemental analysis. 131

Table 21. Octane numbers of MTBE and MIBE gasoline blends. 149

Table 22. Blending research octane number (BRON) and blending motor octane number (BMON) of MTBE and MIBE in gasoline. 150

Table 23. Thermal response factorsof pertinent oxygenated reagents and products. 152

Table 24. Usual GC operating conditions. 153

Table 25. Conversion and selectivity of the liquid-phase ethanol/ isobutanol batch reaction at 100°C as a function of time. 159