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Reaction network of aldehyde hydrogenation over sulfided Ni–Mo/Al_2O_3 catalysts

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Abstract

A reaction network of aldehyde hydrogenation over NiMoS/Al_2O_3 catalysts was studied with aldehydes with straight and branched carbon chains and different chain lengths as feed materials. The reactions in the gas phase and the liquid phase were compared. The main reaction in the aldehyde hydrogenation process is the hydrogenation of the C=O double bond, which takes place over the coordinatively unsaturated sites. The major side reactions are self-condensation of aldehydes and condensation of aldehydes with alcohols. Both reactions involve α-hydrogen and are primarily catalyzed by acid–base bifunctional sites over the exposed Al_2O_3 surfaces.

Keywords: Aldehyde hydrogenation; Sulfided Ni–Mo catalysts; Aldol condensation

1. Introduction

Oxo process alcohols are a major class of organic chemicals [1]. The resulting products from the oxo process may be aldehydes, primary alcohols, or a mixture of the two. Most of these oxo aldehydes are hydrogenated to the corresponding oxo alcohols. A wide range of heterogeneous catalysts is used in the industry to convert aldehydes to alcohols. Although the absence of C=C unsaturation makes the hydrogenation of oxo aldehydes easier, the presence of ppm levels of sulfur in the feed olefin can place serious constraints on the catalyst choice. Sulfided Ni–Mo catalysts, which are known for their hydrogenation and hydrogenolysis activity [2,3], can hydrogenate aldehydes while maintaining their activity in the presence of sulfur compounds, which may be part of the feed stream. Sulfided Ni–Mo and Co–Mo catalysts supported on Al_2O_3 are used extensively in many hydrotreating processes, including hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrogenation (HYD). According to a widely accepted model by Topsøe and co-workers, sulfidation of the oxide phase results in the formation of stacks of MoS_2 slabs over the catalyst surface, and the Ni and Co species are located primarily on the edges of these stacks [4–7]. Active site models based on these structures have been used to account for different product distributions observed in HDS, HDN, and HDO reactions [8–18]. The importance of surface SH or sulfhydryl groups has also been discussed with regard to several reaction mechanisms [17, 19–23]. The evidence for the presence of SH groups has been provided by deuterium exchange studies [24], chemical titration by silver ions [22], Raman spectroscopy [25], and infrared spectroscopy [26]. The Brønsted acidity associated with SH groups in sulfided catalysts was also examined by IR spectroscopy of adsorbed pyridine species [27]. Direct correlations between the HDS activity and SH concentration have also been reported previously [28–32]. The effect of the changes in the surface concentration of Brønsted acid sites and sulfur vacancies on the hydrogenolysis and hydrogenation activities in HDN and HDO reactions have been discussed in the literature [17,19]. Hydrocracking activity of

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the sulfhydryl groups was also reported [33,34]. It has also been proposed that reduced Ni–Mo/Al_2O_3 catalysts may exhibit similar activity, where OH groups act in a manner analogous to that of SH groups, and anion vacancies (CUS) can form during the reduction process as well [19,35,36].

Although the relationships between different active sites, such as coordinatively unsaturated sites (CUS), Brønsted acid sites, and SH and OH groups, over NiMoS and CoMoS catalysts and different reaction steps in HDS, HDN, and HDO reactions are studied extensively, similar correlations in aldehyde hydrogenation reactions have not been the focus of many studies. In our previous articles [37–39], we have reported on the catalytic performance of sulfided Ni–Mo/Al_2O_3 catalysts in the hydrogenation of linear aldehydes to alcohols. The two primary reactions that are of most interest in these reaction schemes are the hydrogenation of the aldehyde to form a corresponding alcohol (the desired reaction) and the formation of heavy products (the undesired reaction). We have also shown that NO and CO_2 could be used as molecules to probe the active sites that promote the hydrogenation and heavy product formation reactions, respectively, as the alcohol formation is correlated with CUS density, whereas the heavy product formation can best be explained by the surface concentration of OH and possibly SH groups.

The focus of this study has been the reaction pathway(s) involved in aldehyde hydrogenation and the relationship between reactions and nature of different surface sites over NiMoS/Al_2O_3 catalysts. Aldehydes with straight and branched carbon chains and different chain lengths were studied as feed materials. The reactions in the gas phase and the liquid phase were compared. Propanal has been used as a model aldehyde for a more detailed analysis of reaction intermediates, products, and side reactions.

2. Experimental

Alumina-supported catalysts with different Mo and Ni loadings were prepared by wet co-impregnation of γ-Al_2O_3 with aqueous solutions of ammonium heptamolybdate and nickel nitrate. The preparation procedure has been presented previously [37,40,41]. The catalyst compositions are reported as weight percentages of the oxide precursors, that is, MoO_3 and NiO, following the convention commonly used in literature. The surface area of samples used in these studies varied between 166 and 195 m^2/g, with pure alumina giving the highest surface area. Before all reaction studies, the catalysts were sulfided in situ at 400 °C with 10% H_2S in H_2 for 10 h followed by He flushing for 1 h at the same temperature before the system was cooled to the desired reaction temperature.

The reaction studies were performed in both the gas phase and the liquid phase. The gas-phase reaction was carried out in a fixed-bed reactor system, which is described in a previous article [37]. We introduced propanal and other probe molecules as feed into the reactor system by saturating a H_2 stream with the use of temperature-controlled bubblers. The concentration of the feed was controlled by the temperature of the bubbler and verified by GC analysis. The outlet of the reactor was connected directly to a condenser with decane as solvent, which was cooled in an ice-water bath. The outlet flow was switched to the condenser after the reaction reached steady state. Condensed species were analyzed by gas chromatography with the use of the liquid auto injector. The lighter components were analyzed on line with the gas injection mode of the GC. The liquid-phase reaction was performed with the Fast Hydrogenation Autoclave Unit (FHAU). The unit consists of two CSTRs, each equipped with dual liquid (oil and water) and hydrogen feed systems, a Robinson–Mahoney stationary catalyst basket, and a heating mantle. The unit was operated in the continuous mode, where only one reactor train was used. The catalyst basket is charged with 6 cm^3 of catalyst. Under each set of conditions, the reactor effluent was collected over a period of 4–6 h and analyzed by an off-line GC equipped with a 60-m boiling point column and FID. All by-products generated from gas-phase and liquid-phase reactions were identified by GC/MS and GC/IR.

TPD experiments were performed with a homemade apparatus, which was previously described [42]. The reactor effluent composition was continually monitored as a function of sample temperature with a mass spectrometer (Hewlett–Packard, MS Engine 5898A). For each of the TPD runs, 30 m^2 (surface area) of sample was loaded into the U-tube quartz reactor. All samples were sulfided in situ by the same procedure as in the reaction studies, that is, 10% H_2S in H_2 was passed over the sample for 10 h at 400 °C, followed by He flushing for 2 h at the same temperature and cooling to 30 °C in He. Propanal adsorption was performed by the introduction of propanal through a diffusion tube with a 30 cm^3 (STP)/min He flow at 30 °C for 1 h. After being flushed with He for 1 h at the same temperature, the samples were heated at a rate of 10 °C/min under a 30 cm^3 (STP)/min He flow.

The conversion of aldehyde ($C\%$) is calculated with the equation

$$C\% = \frac{\text{moles aldehyde in feed} - \text{moles aldehyde in product}}{\text{moles aldehyde in feed}} \times 100.$$

The selectivity of product i is defined as

$$S_i\% = \frac{\text{moles of C in product } i}{\text{moles of C in aldehyde converted}} \times 100.$$

3. Results

3.1. Propanal hydrogenation

Blank reactor runs showed no detectable conversion in the hydrogenation of propanal through an empty reactor

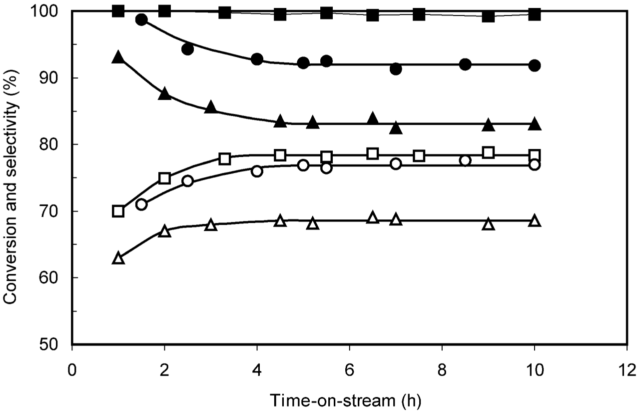


Fig. 1. Conversion and selectivity in propanal hydrogenation over sulfided 3% Ni–15% Mo/Al_2O_3 catalysts (1000 psi, 0.13% propanal in 250 cm^3/min H_2): (■, □) 180, (●, ○) 160, and (▲, △) 140 °C. Bold and blank symbols represent propanal conversion and selectivity to propanol, respectively.

(without catalyst). As can be seen in Fig. 1, where conversion and alcohol selectivity are presented for the first 10 h, reaction over sulfided 3% Ni–15% Mo/Al_2O_3 catalyst reached steady state within the first 5 h. All data presented in this article were collected after steady state was reached.

As expected, propanal conversion increases with increasing reaction temperature. Meanwhile, selectivity for propanol also increases with reaction temperature. However, the difference between 180 and 160 °C is much smaller compared with the difference between 160 and 140 °C. Under the experimental conditions used, the main product is propanol, formed from hydrogenation of the C=O double bond of propanal. Following the definition of “lights and heavies” in hexanal hydrogenation used previously [37], in this article “lights” refers to products with carbon numbers lower than that of the feed, which are produced mainly from full hydrogenation, decarbonylation, and hydrogenolysis/cracking. The term “heavies” refers to products heavier than primary product alcohol, which are produced mainly from self-condensation of aldehydes and condensation of aldehyde with alcohol.

In the process of high-pressure hydrogenation of aldehyde, reaction performance strongly depends not only on the reaction temperature, but also on the feed concentration. From Fig. 2a, it can be seen that selectivity for propanol decreases with feed concentration, whereas the selectivity for heavies increases, suggesting that the formation of heavy products strongly relies on feed concentration. Selectivity for lights, the minor by-products, decreases slightly with increasing feed concentration. Fig. 2b shows propanal conversion rates to be proportional to feed concentration for all temperatures tested. Propanol formation rates, however, do not show a linear dependence on concentration (Fig. 2c), implying that the primary product, propanol, is consumed in secondary reactions.

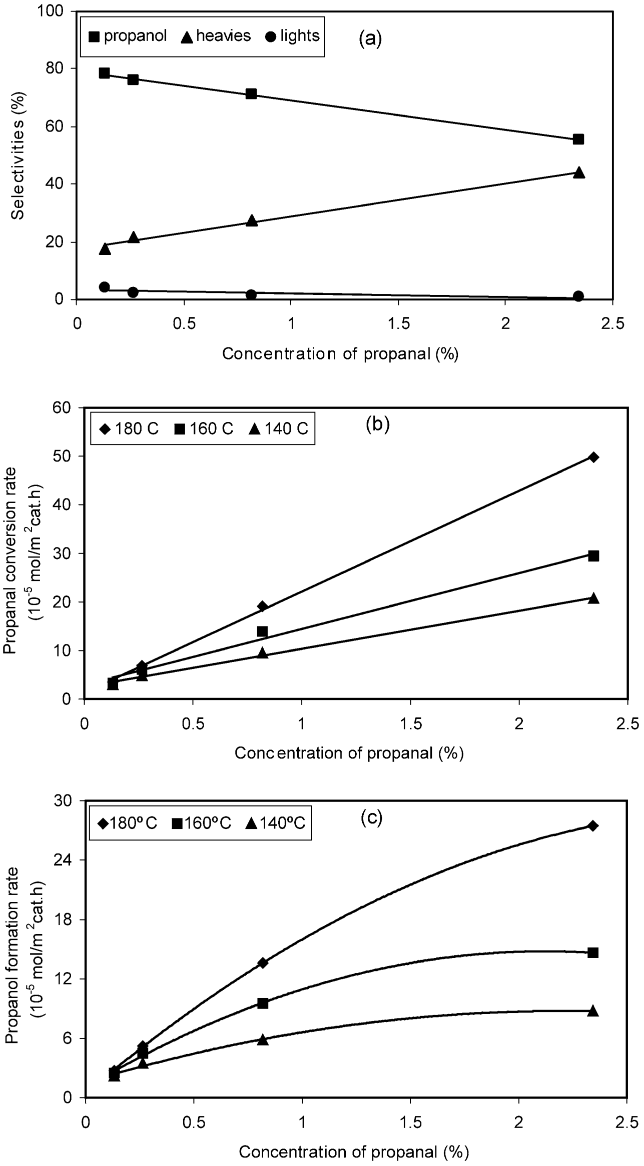


Fig. 2. Effect of feed concentration on propanal hydrogenation performance over sulfided 3% Ni–15% Mo/Al_2O_3 catalysts (1000 psi, 250 cm^3/min H_2): (a) selectivities at 180 °C, (b) propanal conversion rates at different temperatures, and (c) propanol formation rates at different temperatures.

3.2. *Effect of structure and chain length of the aldehyde molecule in the hydrogenation reaction*

To gain insight into the mechanistic steps involved in aldehyde hydrogenation reactions, four different aldehyde molecules were tested: propanal, hexanal, 2-ethyl-butanal, and 2-methyl-pentanal. The objective was to examine the effect of chain length and to compare the linear aldehydes to branched aldehydes in hydrogenation reactions over sulfided Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 catalysts.

3.2.1. *Hydrogenation of propanal and hexanal*

Fig. 3 shows the catalytic performance of sulfided Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 catalysts in the hydrogena-

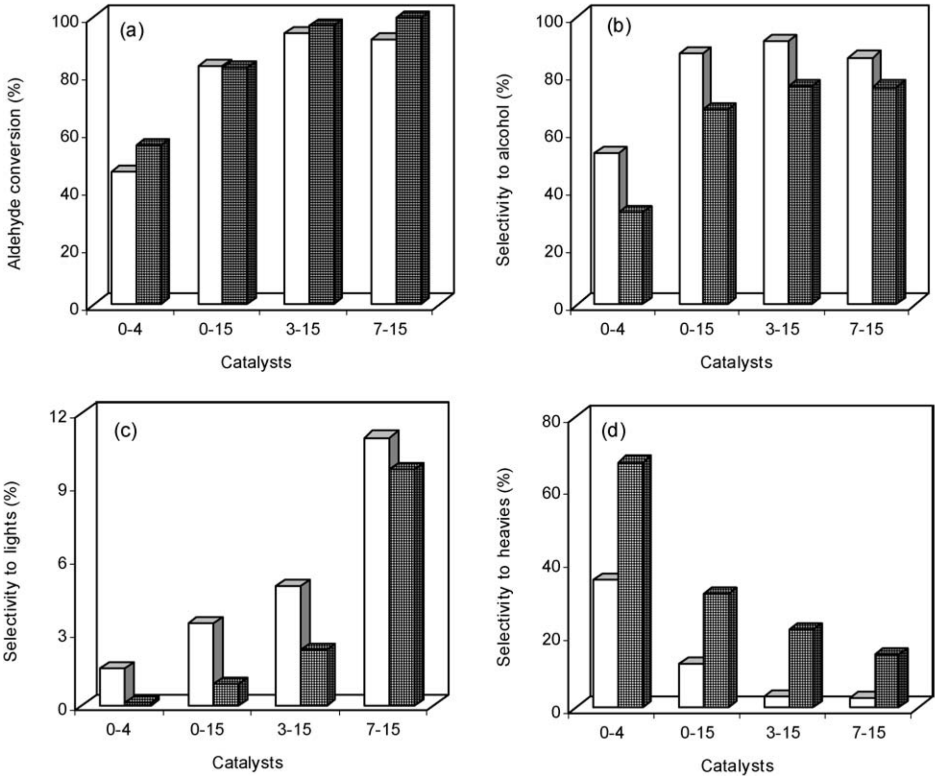


Fig. 3. Effect of catalyst composition (% NiO–% MoO_3/Al_2O_3) on performance in hexanal and propanal hydrogenation at 180 °C: (☐) hexanal (0.09%), (■) propanal (0.26%). (a) Conversion, (b) selectivity to alcohol, (c) selectivity to lights, and (d) selectivity to heavies.

tion of propanal and hexanal at the same reaction temperature of 180 °C and a reaction pressure of 1000 psi. To make a comparison of product distributions at similar conversion levels for the two feed molecules, we obtained the data in these figures at propanal and hexanal concentrations of 0.26 and 0.09%, respectively (Fig. 3a).

Both propanal and hexanal conversions and selectivities for alcohols increase with Mo loading over mono-metallic catalysts. Although Ni addition increases the conversion, further increases in Ni content do not change conversion or alcohol selectivity very noticeably. For both aldehydes, the selectivity for lights increases with increasing Mo content, and the selectivity for heavies decreases. The effect of Ni content is much more pronounced for light product selectivity than it is for heavy product selectivity. Although the trends for the two aldehyde molecules are quite similar, the alcohol selectivity for hexanal is significantly higher than it is for propanal. Another major difference between the two feed molecules is that the selectivity for heavies for propanal is much higher, whereas the selectivity for lights is lower. It is conceivable that the longer chains can undergo cracking more readily, giving rise to more lights production. The higher heavy product selectivities observed for propanal hydrogenation imply that smaller aldehydes can undergo condensation-type side reactions more easily. However, the difference in heavy selectivities can also be explained by the different feed concentrations, as mentioned in the previous section.

3.2.2. *Effect of temperature on the hydrogenation of hexanal and 2-ethyl-butanal*

The effect of temperature on selectivities for two different aldehyde molecules, hexanal and 2-ethyl-butanal, is presented in Fig. 4. The two molecules chosen have the same carbon number, but one is linear and the other has a branched structure. Experiments were carried out over sulfided 3% Ni–15% Mo/γ-Al_2O_3 catalysts at a temperature range of 140–180 °C and 1000 psi H_2. The aldehyde concentration was kept at 0.8–0.9%. Although the conversions of the two aldehyde feed molecules are comparable, the selectivity trends observed are not very similar. The alcohol selectivity increases with temperature for hexanal, whereas it is seen to decrease for 2-ethyl-butanal. The selectivities for light and heavy products are also quite different for the branched and linear aldehydes. The selectivity for lights is much higher for the branched molecule, with a sharp increase with increasing temperature. The same selectivity for the linear molecule, on the other hand, is much lower and shows only a small increase with increasing temperature. The trends for the heavy products are exactly the opposite of those seen for the light products. The linear aldehyde shows a much higher selectivity for heavy products, which decreases sharply with increasing temperature. The branched molecule, on the other hand, shows very little heavy product formation, with little temperature sensitivity. The calculated apparent activation energies are 11 and 9 kcal/mol for the hydrogenation of hexanal and 2-ethyl-butanal, respectively.

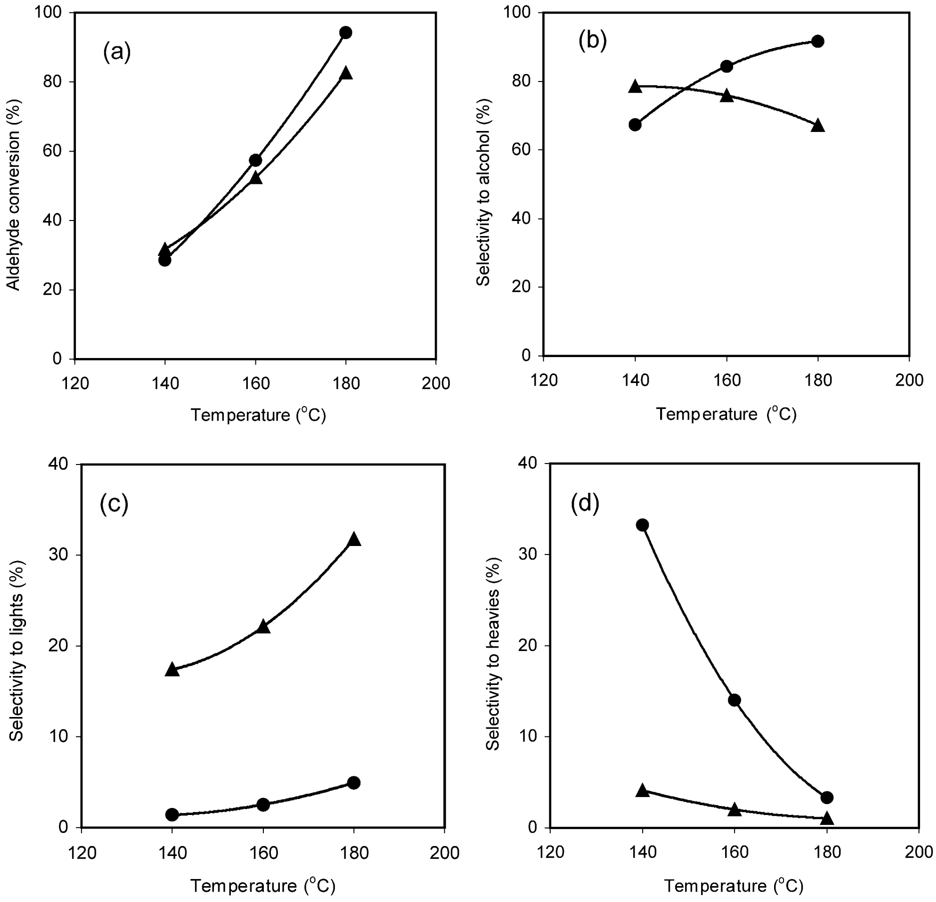


Fig. 4. Effect of temperature on performance of hexanal and 2-ethyl-butanal hydrogenation over sulfided 3% Ni–15% MoO_3/Al_2O_3 catalysts. (a) Conversion of aldehyde, (b) selectivity to alcohol, (c) selectivity to lights, and (d) selectivity to heavies; (●) hexanal (0.09%), (▲) 2-ethyl-butanal (0.08%).

Table 1

Comparison of hydrogenation of propanal, hexanal, 2-ethyl-butanal, and 2-methyl-pentanal over sulfided 3% Ni–15% Mo/Al_2O_3 catalysts[a]

Feed molecule	*C* %[b]	*S* %[c]		
	Aldehyde	Alcohol	Lights	Heavies
Propanal	99.7	78.4	4.0	17.6
Hexanal	94.2	87.3	4.6	8.1
2-Ethyl-butanal	82.6	67.1	31.8	1.1
2-Methyl-pentanal	58.9	86.2	8.4	5.4

[a] Reaction conditions: $T = 180\,^\circ\mathrm{C}$, 1000 psi, 250 cm^3 (STP)/min H_2; concentration of aldehyde: propanal = 0.13%, hexanal = 0.09%, 2-ethyl-butanal = 0.08%, 2-methyl-pentanal = 0.10%.

[b] *C*%—conversion.

[c] *S*%—selectivity.

For the branched molecule, cracking reactions are likely to play a more important role in the overall conversion of the aldehyde compared with the linear molecule. Therefore, the difference in the activation energies does not necessarily imply a difference in the intrinsic activation energy of the C=O hydrogenation reaction, but it may simply be due to a contribution from the cracking reaction for the branched molecule.

Table 1 shows a comparison of four different aldehyde molecules, propanal, hexanal, 2-methyl-pentanal, and 2-ethyl-butanal, under similar conditions. The effect of chain length and branched structure on the conversion of aldehyde and selectivity for by-products are as follows:

- Conversion of aldehyde:
  propanal > hexanal > 2-ethyl-butanal > 2-methyl-pentanal.
- Selectivity for heavies:
  propanal > hexanal > 2-methyl-pentanal > 2-ethyl-butanal.
- Selectivity for lights:
  propanal < hexanal < 2-methyl-pentanal < 2-ethyl-butanal.

3.3. *Comparison of reactions in liquid phase and gas phase*

Liquid-phase reaction of hexanal hydrogenation was performed in a CSTR unit. The products obtained from liquid-phase reaction and gas-phase reaction (condensed in decane) were analyzed by gas chromatography with a 60-m boiling point column and FID. The sample chromatograms from liquid-phase and gas-phase reaction experiments were very similar, indicating that the products obtained from the gas-phase and liquid-phase reaction studies are the same. Detailed identification of the product species was achieved by

GC/MS and GC/IR analyses. The main by-products consisted of acetals, dimer aldehydes and alcohols, dimer ethers, esters, acids, and oxygenated trimers and tetramers.

The effect of reaction temperature at different space velocities on the performance of hexanal hydrogenation in the liquid phase is shown in Fig. 5. The conversion increases almost linearly with temperature at the highest space velocity used. This trend is not as apparent at lower space velocities, since conversion approaches 100% at higher temperatures. The apparent activation energy for liquid-phase reactions is around 7 kcal/mol. The fact that it is somewhat lower than the activation energy obtained in the gas phase raises the question about possible mass transfer limitations in the liquid phase. Alcohol selectivities for different space velocities are presented in Fig. 5b. The space velocities for both liquid-phase and gas-phase reaction experiments are expressed as LHSV for purposes of comparison. Alcohol selectivity increases with increasing temperature for both liquid phase and gas phase. It is also interesting to note that the selectivities obtained at the same temperature are very close to one another for both liquid and gas phases when space velocities are comparable. The similarities between the trends observed in the gas phase and the liquid phase are reassuring, since they imply that the experimental results obtained in the gas phase are still relevant for industrial applications of similar reactions, which use primarily liquid feeds.

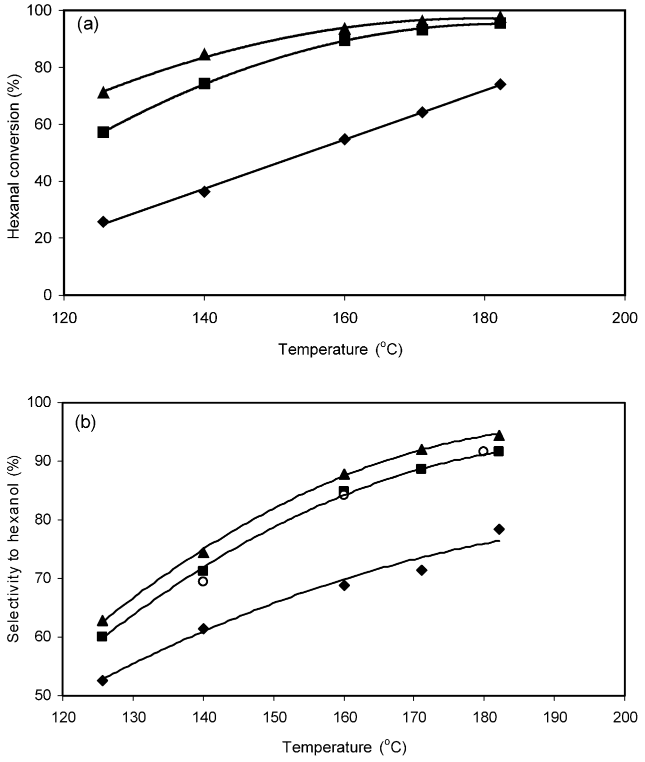


Fig. 5. Effect of temperature and space velocity on hexanal conversion (a) and selectivity to hexanol (b) in hexanal hydrogenation at liquid phase over sulfided 3% Ni–15% MoO_3/Al_2O_3 catalyst: (◆) SV (12 h^{-1}), (■) SV (3.8 h^{-1}), and (▲) SV (2.0 h^{-1}); gas phase results are included for comparison ((○) SV (0.8 h^{-1})). (a) Conversion of aldehyde, (b) selectivity to alcohol.

The effect of water addition was also examined in both liquid-phase and gas-phase reactions. Table 2 clearly shows that under identical conditions, higher alcohol selectivities are obtained when water is introduced into the feed. This observation holds for both liquid and gas phases and for both hexanal and propanal feeds. It is possible that water, by acting as a base, may be neutralizing the OH groups on the Al_2O_3 surface that are mainly responsible for the heavy product formation. The effect of H_2O addition on the main by-products in the liquid-phase reaction, identified by GC/MS and GC/IR, is presented in Fig. 6. The heavies that were significantly reduced with water addition are dimers (C_{12} aldehydes and alcohols), esters, trimers, and tetramers.

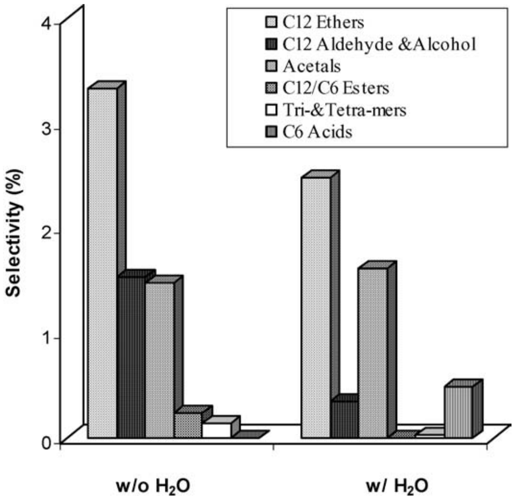


Fig. 6. Effect of H_2O in the feed on formation of by-products in hexanal hydrogenation at liquid phase over sulfided 3% Mo–15% Mo/Al_2O_3 catalysts.

Table 2
Effect of H_2O on hydrogenation of hexanal and propanal (sulfide 3% Ni–15% Mo/Al_2O_3 catalyst)

Condition[a]	Hexanal liquid phase[b]		Hexanal gas phase[c]		Propanal gas phase[d]	
	C%	*S*%	*C*%	*S*%	*C*%	*S*%
W/O H_2O	97.6	91.3	98.5	88.3	53.7	55.6
W/ H_2O	97.5	93.9	94.7	94.7	51.6	57.4

[a] Reaction temperature 180 °C, H_2 pressure 1000 psi.
[b] Space velocity 2.0 h^{-1}, concentration of hexanal and H_2O, 20 and 0.60%.
[c] Space velocity 1.2 h^{-1}, concentration of hexanal and H_2O, 0.52 and 0.24%.
[d] Space velocity 0.4 h^{-1}, concentration of propanal and H_2O, 0.25 and 0.02%.

Table 3
Product distribution of propanal hydrogenation over sulfided 7% Ni–15% Mo/Al_2O_3 catalyst[a]

Product	Selectivity (%)		
	140 °C	160 °C	180 °C
Ethane	–	0.1	0.4
Propane	0.3	1.0	2.4
Propanol	29.2	38.6	57.4
2-Methyl-pentane	–	0.2	1.2
2-Methyl-pentene	4.4	3.4	1.1
2-Methyl-2-pentene	4.6	5.2	3.1
Propyl ether	0.4	0.7	2.0
Propionic acid	0.6	0.5	0.3
2-Methyl-pentanal	49.1	39.8	13.4
Propyl-propionate	–	–	0.5
2-Methyl-2-pentenal	5.6	0.2	0.03
Propionaldehyde dipropyl acetal	–	–	0.03
2-Methyl-pentanol	0.7	5.2	12.5
2-Methyl-pentenol	0.4	0.2	0.1
Trimers	5.2	5.3	5.3
Conversion of propanal (%)	13.6	25.4	53.7

[a] Reaction conditions: 1000 psi, 0.35% propanal, 250 cm^3 (STP)/min H_2, 12.5 m^2 catalyst.

The addition of water, however, appears to produce more acids. It is also noted that the presence of water in the feed results in a decrease in the overall aldehyde conversion, since H_2O may inhibit the vacancy sites by adsorption and/or oxidation.

3.4. Reaction studies using intermediate and product species as probe molecules

Since our previous experiments showed that propanal and hexanal exhibit the same trends in hydrogenation reactions, further studies to elucidate the reaction networks were conducted with C_3 aldehydes and their intermediates or products. Propanal, which can be representative of the straight-chain aldehydes, better facilitates an examination of the effect of intermediate species through easier analysis and identification of all products. Reactions of probe molecules were studied over a sulfided bimetallic catalyst, 7% Ni–15% Mo/γ-Al_2O_3.

3.4.1. Propanal hydrogenation

Table 3 shows the product distribution of propanal hydrogenation over sulfided 7% Ni–15% Mo/γ-Al_2O_3 catalyst at a temperature range of 140–180 °C. The main products from propanal hydrogenation at low reaction temperatures are propanol, 2-methyl-pentanal, 2-methyl-pentenal, methyl-pentenes, and trimers. Major products at high temperature are propanol, 2-methyl-pentanal, 2-methyl-pentanol, and hydrocarbons. No significant change in selectivity for trimers is observed.

3.4.2. Effect of propanol on propanal hydrogenation

When the reactivity of propanol was examined under the conditions used for propanal hydrogenation, the conversion of alcohol was seen to be very low (Table 4). The main products are propane from hydrogenation of propanol and propyl ether from bimolecular dehydration of two propanol molecules. The trace amounts of ethane and methyl-propyl ether observed are likely to result from cracking of propyl ether. At higher temperatures, isopropanol appears because of the isomerization of propanol, possibly catalyzed by acidic sites (–OH, –SH). The comparison presented in Table 5, however, shows that the effect of propanol on propanal hydrogenation cannot be ignored. The presence of alcohol in the feed causes a significant decrease in aldehyde conversion, suggesting a strong inhibition effect. The product distributions in this table are presented as flow rates since the presence of alcohol in the feed makes the use of a "selectivity" concept difficult.

Table 4
Reaction of propanol over sulfided 7% Ni–15% Mo/Al_2O_3[a]

Product	Selectivity of products (%)		
	140 °C	160 °C	180 °C
Ethane	3.9	3.7	4.4
Propane	54.1	53.2	52.0
Iso-propanol	–	–	1.7
Methyl-propyl ether	9.0	9.4	14.1
Propyl ether	33.1	33.4	27.9
Conversion of propanol (%)	0.3	3.0	8.0

[a] Reaction conditions: 1000 psi, 0.05% propanol in 250 cm^3 (STP)/min H_2, 12.5 m^2 catalyst.

The amounts of 2-methyl-pentanal and trimers increase significantly because of the enhancement of the reaction between propanal and propanol. The 2-methyl-2-pentenal and 2-methyl-2-pentenol yields decrease, possibly because of the inhibition effect from adsorbed propanol on the self-condensation reaction of propanals.

3.4.3. Reaction of 2-methyl-pentanal

2-Methyl-pentanal is one of the major by-products of propanal hydrogenation. Table 6 shows the reaction results obtained when 2-methyl-pentanal is used as a feedstock over sulfided 7% Ni–15% Mo/γ-Al_2O_3 catalyst. At 180 °C, the conversion of 2-methyl-pentanal is quite high, and the main reaction is hydrogenation of aldehyde to the corresponding alcohol. 2-Methyl-pentane and 2-methyl-pentyl ether, which are seen in small amounts, result from the hydrogenation of 2-methyl-pentanol and dehydration of 2-methyl-pentanol, respectively. Propane may come from cracking of 2-methyl-pentanal and 2-methyl-pentanol molecules.

3.4.4. Reaction of 2-methyl-pentanol

2-Methyl-pentanol is the other major by-product of the propanal hydrogenation process, especially at higher reaction temperatures. When it is used as the feed molecule over sulfided 7% Ni–15% Mo/γ-Al_2O_3 catalyst, the only major reaction observed is the hydrogenation of alcohol to produce the corresponding hydrocarbon, 2-methyl-pentane (Table 7). Other products are propane and trace quantities of ethers.

Table 5
Product flow rates (mol/h × 10^7) in propanal hydrogenation (w/ and w/o propanol) over sulfided 7% Ni–15% Mo/Al_2O_3 catalyst[a]

Product	Without propanol			With propanol		
	140 °C	160 °C	180 °C	140 °C	160 °C	180 °C
Ethane	–	0.1	1.2	–	0.1	0.6
Propane	0.2	0.9	5.1	0.4	0.8	4.3
Propanol	15.6	38.3	120.3	42.6	52.3	116.0
2-Methyl-pentane	–	0.1	1.2	–	–	0.6
2-Methyl-pentene	0.8	1.8	1.2	1.4	1.8	1.8
2-Methyl-2-pentene	1.2	2.5	3.3	1.7	2.3	4.3
Propyl ether	0.2	0.4	2.2	0.3	0.5	1.0
Propionic acid	0.4	0.4	0.8	0.8	0.4	0.8
2-Methyl-pentanal	13.1	19.7	14.1	16.0	21.1	20.7
Propyl-propionate	–	–	0.4	0.4	0.2	0.6
2-Methyl-2-pentenal	1.6	0.1	trace	1.4	trace	–
Propionaldehyde dipropyl acetal	–	–	trace	1.4	0.1	0.1
2-Methyl-pentanol	0.2	2.5	13.1	1.4	2.5	11.3
2-Methyl-pentenol	0.1	0.1	0.1	–	–	–
Trimers	0.9	1.7	3.7	2.5	3.8	6.1
Conversion of propanal (%)	13.6	25.4	53.7	9.8	14.5	39.0

[a] Reaction conditions: 1000 psi, 250 cm^3 (STP)/min H_2, 12.5 m^2 catalyst, propanal flow rate in feed = 391 × 10^{-7} mol/h, propanol flow rate in feed = 56 × 10^{-7} mol/h. Trace means < 0.1 in the table.

Table 6
Reaction of 2-methyl-pentanal over sulfided 7% Ni–15% Mo/Al_2O_3 catalyst[a]

Product	Selectivity (%)
Propane	2.0
2-Methyl-pentane	3.1
2-Methyl-pentanol	90.3
2-Methyl-pentyl ether	4.7
Conversion of propanal (%)	62.4

[a] Reaction conditions: 180 °C, 1000 psi, 0.05% 2-methyl-pentanal in 250 cm^3 (STP)/min H_2, 25 m^2 catalyst.

Table 7
Reaction of 2-methyl-pentanol over sulfided 7% Ni–15% Mo/Al_2O_3 catalyst[a]

Product	Selectivity (%)
Propane	9.9
2-Methyl-pentane	89.1
4-Methyl-pentyl propyl ether	0.4
2-Methyl-pentyl ether	0.6
Conversion of propanal (%)	36.2

[a] Reaction conditions: 180 °C, 1000 psi, 0.02% 2-methyl-pentanol in 250 cm^3 (STP)/min H_2, 25 m^2 catalyst.

3.4.5. *Reaction of 2-methyl-pentenal*

2-Methyl-pentenal is one of the major by-products at lower temperatures in the propanal hydrogenation network. Results from the reaction of 2-methyl-pentenal over sulfided 7% Ni–15% Mo/γ-Al_2O_3 catalyst are presented in Table 8. 2-Methyl-pentanal and 2-methyl-pentanol are the main products in this reaction. In addition, hydrocarbons, such as 2-methyl-pentane, 2-methyl-pentene, and 2-methyl-2-pentene, are also produced. 2-Methyl-pentenol is also observed.

Table 8
Reaction of 2-methyl-pentenal over sulfided 7% Ni–15% Mo/γ-Al_2O_3 catalyst[a]

Product	Selectivity of products (%)		
	140 °C	160 °C	180 °C
Propane	0.1	0.1	0.1
2-Methyl-pentane	0.3	0.7	2.0
2-Methyl-pentene	7.2	7.9	8.1
2-Methyl-2-pentene	5.2	7.1	8.9
2-Methyl-pentanal	54.4	54.7	59.3
Propyl-propionate	–	–	0.5
2-Methyl-pentanol	30.3	27.3	19.5
2-Methyl-pentenol	1.2	1.0	0.8
Others	1.2	1.2	1.3
Conversion of propanal (%)	56.1	63.5	89.5

[a] Reaction conditions: 1000 psi, 0.11% 2-methyl-pentenal in 250 cm^3 (STP)/min H_2, 25 m^2 catalyst.

3.4.6. *Reaction of acetal*

A trace amount of propionaldehyde dipropyl acetal was observed in the propanal hydrogenation reaction. Since propionaldehyde dipropyl acetal was not available, the reaction experiments were performed with propionaldehyde diethyl acetal to examine the reactivity of these acetals over the sulfided Ni–Mo catalysts used in this study. The reaction results, which are summarized in Table 9, show high reactivity. The main products are ethanol and ethers, which are produced from hydrogenolysis and cracking of acetal.

3.4.7. *Reaction of propyl ether*

A small amount of propyl ether was observed in propanal hydrogenation. Reaction of ether as a feed over the same catalyst showed a moderate conversion, and the main products were propane and propanol (Table 10).

Table 9
Reaction of propionaldehyde diethyl-acetal over sulfided 7% Ni–15% MoO_3/Al_2O_3 catalyst[a]

Product	Selectivity (%)	
	140 °C	180 °C
Ethane	0.8	4.1
Propane	0.5	5.0
Ethanol	35.8	40.9
Propanal	0.3	0.3
Iso-propanol	0.6	6.4
Propanol	0.3	0.7
Methyl ether	0.3	5.2
Methyl-ethyl ether	7.2	17.0
Ethyl-propyl ether	32.5	9.0
Allyl ethyl ether	14.9	3.1
Others	7.6	8.5
Conversion of acetal (%)	47.5	94.7

[a] Reaction conditions: 1000 psi, 0.02% propionaldehyde diethyl acetal, 250 cm^3 (STP)/min H_2, 12.5 m^2 catalyst.

Table 10
Reaction of propyl-ether over sulfided 7% Ni–15% Mo/Al_2O_3 catalyst[a]

Product	Selectivity (%)	
	140 °C	180 °C
Ethane	4.9	2.3
Propane	48.7	72.0
Propanal	–	0.1
Iso-propanol	8.3	1.1
Propanol	12.0	14.8
Methyl ether	11.7	3.7
Methyl-propyl ether	5.1	4.5
Ethyl-propyl ether	4.7	1.1
Others	4.7	0.5
Conversion of propyl-ether (%)	1.1	14.3

[a] Reaction conditions: 1000 psi, 0.03% propyl ether in 250 cm^3 (STP)/min H_2, 12.5 m^2 catalyst.

Table 11
Reaction of propanal over sulfided Al_2O_3 support[a]

Product	Selectivity of products (%)		
	140 °C	160 °C	180 °C
Propanol	0.5	0.7	1.1
Propyl ether	–	0.3	0.4
2-Methyl-pentanal	0.6	0.9	1.3
Propyl-propionate	–	0.6	0.5
2-Methyl-2-pentenal	97.8	96.3	95.2
Trimers	1.1	1.3	1.5
Conversion of propanal (%)	8.8	18.9	27.8

[a] Conditions: 1000 psi, 0.35% propanal in 250 cm^3 (STP)/min H_2, 12.5 m^2 γ-Al_2O_3.

Table 12
Product flow rates (mol/h $\times 10^7$) in propanal reaction (w/ and w/o propanol) over sulfided Al_2O_3 support[a]

Product	Without propanol	With propanol
Lights	–	1.2
Iso-propanol	–	0.8
Propanol	1.2	30.7
Cycle-propane	–	12.9
Ethers	0.2	18.4
Propionic acid	–	13.3
2-Methyl-pentanal	0.7	10.2
Propyl-propionate	0.3	8.2
2-Methyl-2-pentenal	51.7	6.8
Propionaldehyde dipropyl acetal	–	2.2
Trimers	0.5	2.3
Conversion of propanol (%)		44.9
Conversion of propanal (%)	27.8	26.0

[a] Reaction conditions: 1000 psi, 250 cm^3 (STP)/min H_2, 12.5 m^2 γ-Al_2O_3, propanal flow rate in feed = 391×10^{-7} mol/h, propanol flow rate in feed = 56×10^{-7} mol/h.

3.5. Effect of support and catalyst composition on aldehyde reaction network

3.5.1. Role of the support

To assess the role of the support in the reaction network, we performed propanal hydrogenation experiments over a bare support, which was sulfided by the same procedure that was used for catalysts. Table 11 clearly shows that a sulfided γ-Al_2O_3 support has significant activity in converting propanal. The major product is 2-methyl-pentenal, which results from aldol condensation of propanals. Its selectivity is over 95% in the temperature range of 140–180 °C. The second highest selectivity is for trimers. The hydrogenation activity is negligible, with only trace amounts of propanol produced. Propyl-propionate appears at higher temperatures.

The effect of propanol on the reaction of propanal over sulfided γ-Al_2O_3 support is presented in Table 12. The product distributions in this table are presented as flow rates. Unlike the conversion over the catalyst, the propanol conversion is much higher over the support. It should be noted that the propanol conversion reported is the "apparent" conversion, since propanol could also be formed from the reaction of the aldehyde. However, the propanol formation over the support is expected to be quite small, making the "apparent" conversion of propanol close to the real conversion. The conversion of propanal does not appear to have been affected significantly by the presence of alcohol in the feed. The main products are 2-methyl-pentanal, which is the result of condensation of propanal and propanol, and propyl ether, which results from the reaction of two propanol molecules. The other products are propyl-propionate and propionic acid. Acetals and some trimers are also among the products. An important effect of the presence of alcohol is seen in the decreased yield of 2-methyl-pentenal. Reaction between two aldehyde molecules is somewhat hindered by reaction between aldehyde and alcohol molecules, as reflected in the increased products of propyl-propionate, 2-methyl-pentanal, and propyl ether.

3.5.2. Effect of catalyst composition

The effect of metal loading on product distribution in propanal hydrogenation over sulfided (Ni)Mo/γ-Al_2O_3 cat-

Table 13
Effect of metal loading on product distribution in propanal hydrogenation over sulfided catalysts[a]

Products	% NiO–% MoO_3/Al_2O_3 catalysts				
	0–4	0–10	0–15	3–15	7–15
Ethane	0.1	0.1	0.1	0.5	2.2
Propane	0.1	0.6	0.8	1.8	7.5
Propanol	32.3	56.3	67.6	76.1	75.9
2-Methyl-pentane	–	0.1	0.1	1.5	1.8
2-Methyl-pentene	1.6	2.8	3.6	1.8	0.1
2-Methyl-2-pentene	7.2	4.5	6.3	2.1	0.1
Propyl ether	0.4	0.4	0.2	0.2	1.4
Propionic acid	0.2	0.4	–	–	–
2-Methyl-pentanal	10.7	9.9	6.1	2.8	1.8
Propyl-propionate	1.2	0.3	–	–	–
2-Methyl-2-pentenal	2.3	0.6	–	–	–
Propionaldehyde dipropyl acetal	1.0	–	–	–	–
2-Methyl-pentanol	32.8	21.0	12.4	11.8	7.7
2-Methyl-2-pentenol	2.2	0.7	0.6	0.3	0.2
Trimers	8.0	2.4	2.2	1.0	1.3
Conversion of propanal (%)	55.3	76.1	82.7	97.2	99.6

[a] Reaction conditions: 1000 psi, 180 °C, 0.26% propanal 250 cm^3 (STP)/min, 25 m^2 catalyst.

alysts is presented in Table 13. It can be seen that, with increasing Mo loading, that hydrogenation activity increases significantly. It appears that conversion of propanal and selectivity for propanol increase markedly, whereas the selectivity for hydrocarbons, which mainly result from cracking and full hydrogenation over CUS, shows a more gradual increase. Meanwhile, the selectivity for heavy O-containing species (e.g., 2-methyl-pentanal, 2-methyl-pentanol), which are mainly produced from the reactions over the exposed γ-Al_2O_3 surface, decreases pronouncedly. With the addition of Ni, the conversion of propanal and selectivity for propanol are enhanced further. Selectivity for heavy O-containing products decreases, whereas the selectivity for light hydrocarbons increases, especially at higher Ni loading.

3.6. *Propanal TPD studies on sulfided Al_2O_3 support and NiMo/γ-Al_2O_3 catalyst*

Propanal TPD experiments were carried out over sulfided 3% Ni–15% Mo/γ-Al_2O_3 catalyst and sulfided γ-Al_2O_3 support. Propanal was adsorbed at room temperature, and the species eluting from the surface as a function of temperature were monitored by GC/MS with the scan mode. Analysis of individual ions shows that over both the catalyst and the support, the primary species formed during TPD experiments is 2-methyl-2-pentenal ($m/z = 41$). 2-Methyl-pentanal/ol ($m/z = 43$) and propanol ($m/z = 31$) are also observed in trace quantities. The desorbed species are propanal ($m/z = 29$) and H_2O ($m/z = 18$). H_2S ($m/z = 34$) desorption is also observed, but only from the catalyst and not from the support, indicating that Al_2O_3 cannot be sulfided. This result is consistent with our previous observations with TPD/TPR [17] and XPS [37]. The TPD profile obtained over the Al_2O_3 support shows one broad propanal ($m/z = 29$) desorption feature centered at 117 °C (Fig. 7). The adsorption sites are the OH groups on the Al_2O_3 surface. The profile obtained from the catalyst shows two major propanal desorption features at 95 °C and 158 °C. The peak at the lower temperature may represent propanal desorbing from the exposed Al_2O_3 surface and/or Brønsted acid sites associated with Mo centers. The desorption temperature (95 °C), which is lower for the catalyst than it is for the Al_2O_3 support (117 °C), may imply that the adsorption of propanal on Brønsted acid sites is weaker than that on OH groups over the Al_2O_3 surface. The broad peak at higher temperatures (around 150 °C) indicates the propanal desorbing from CUS. The broad high-intensity peak of 2-methyl-2-pentenal ($m/z = 41$) observed over the alumina support is consistent with the reaction network with regard to aldol condensation of propanal, which is the major reaction of propanal over the Al_2O_3 support (Fig. 7). NiMo/Al_2O_3 catalyst shows two desorption features for 2-methyl-2-pentenal. The one at 133 °C is likely to stem from Brønsted acid sites associated with Mo sites. The other one formed at OH groups on the Al_2O_3 surface appears at the same temperature as the peak seen over the Al_2O_3 support; however, the intensity is much weaker.

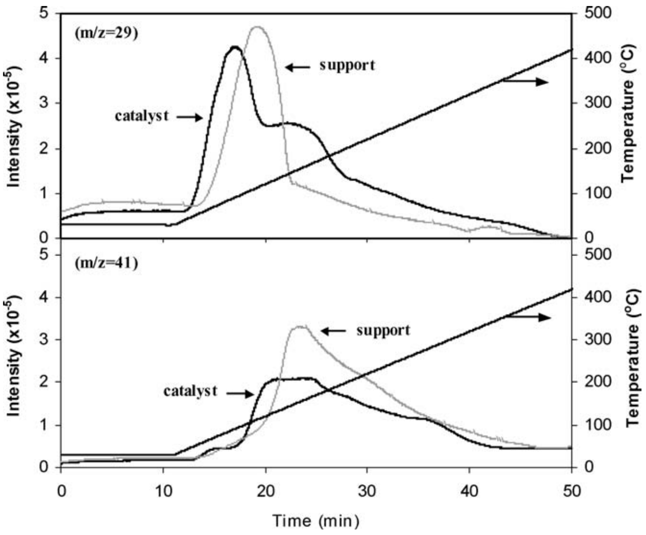
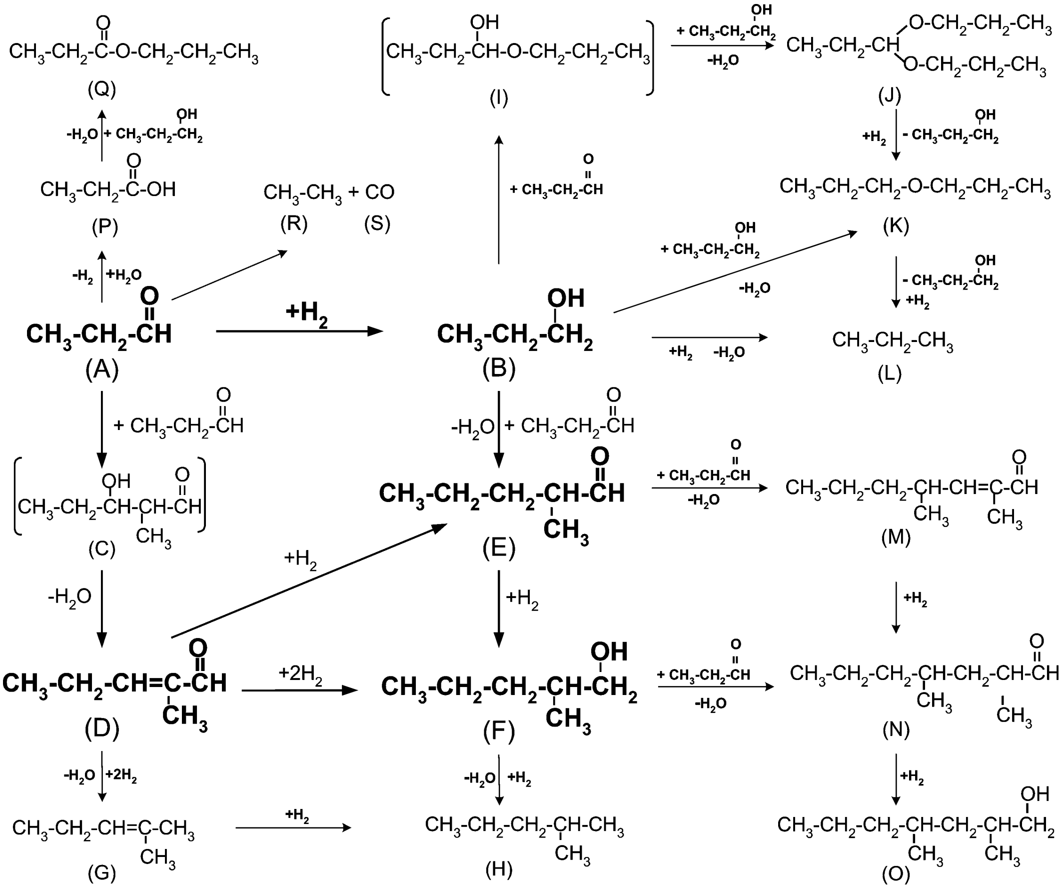


Fig. 7. Propanal TPD profiles over sulfided 3% Ni–15% Mo/Al_2O_3 catalyst and sulfided Al_2O_3 support.

4. Discussion

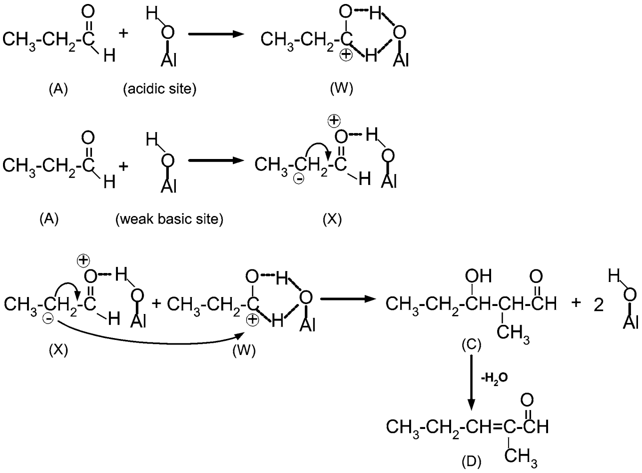
Reaction experiments using various probe molecules provide important clues about the reaction network involved in the hydrogenation of aldehydes over sulfided NiMo/Al_2O_3 catalysts. It appears that the primary steps involved in the hydrogenation of aldehydes are similar regardless of the length of carbon chain, as seen from the similarity in the trends observed for propanal and hexanal. The reaction networks for the liquid-phase and gas-phase systems are also similar, as indicated by the similarity of the product distributions. The



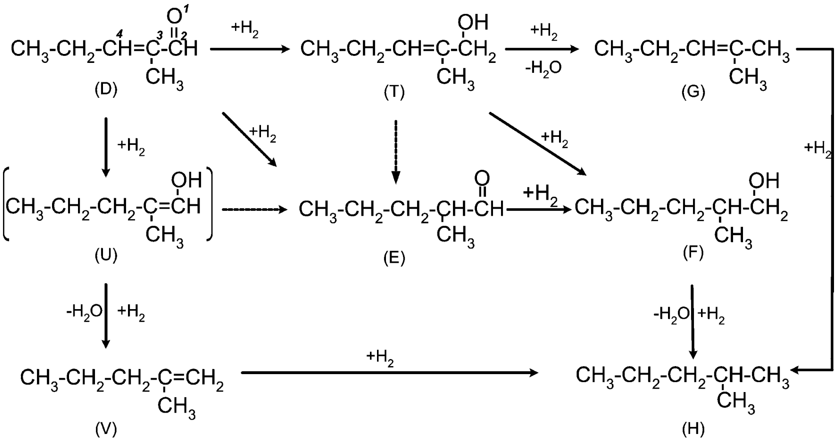
Scheme 1. Proposed reaction network of propanal hydrogenation over NiMoS/γ-Al_2O_3 catalyst.

primary steps involved in the propanal (A) hydrogenation network may be envisioned as in Scheme 1. The main reaction is hydrogenation of the C=O double bond to form the corresponding alcohol (B). Over the sulfided $NiMo/Al_2O_3$ catalysts, the primary hydrogenation sites are coordinatively unsaturated sites (CUS), that is, anionic vacancies associated with Mo or Ni centers. Our earlier studies on HDN and HDO catalysis have shown Mo-associated anionic vacancies to have substantial hydrogenation activity, but the intrinsic activity of the Ni-associated CUS sites is much higher [17,41]. The results from our present investigation suggest that the conclusions derived earlier about the hydrogenation function of the NiMoS catalysts hold for aldehyde hydrogenation reactions as well. The correlations observed between the NO adsorption capacities of these catalysts and the alcohol formation rates provide further evidence about the role of anion vacancies in the transformation of aldehydes to alcohols [37–39].

One of the major side reactions is aldol condensation of two aldehyde molecules. Aldol condensation reactions, which are used for the production of many fine chemicals, are primarily base-catalyzed [43, and references therein]. However, acid–base bifunctional catalysts can also promote aldol condensation reactions [44–47]. The existence of OH groups with different acidities/basicities was demonstrated with the DRIFTS technique and is reported in our previous articles [37,38]. Over alumina support, therefore, aldol condensation is likely to occur, making use of the bifunctionality of the OH groups (Scheme 2). The weak acid sites can activate the carbonyl group through polarization of the C–O bond, which leaves carbon of the aldehyde group with a higher positive charge density (W). The basic sites, on



Scheme 2. Proposed mechanism for aldol condensation of propanals over acid–base sites.



Scheme 3. Proposed network for hydrogenation of α,β-unsaturated aldehyde.

the other hand, can form enolate ions (X), which can act as carbon nucleophiles (carbanion) and attack the positively charged carbon of the intermediate formed on the acidic sites. The aldol intermediate (C) can then lose water and form a α,β-unsaturated carbonyl compound (D). As seen in Table 11, the main species formed over the bare alumina support is the product of this reaction, namely 2-methyl-2-pentenal.

Whereas "self-condensation" is an important side reaction in the hydrogenation network of linear aldehydes, reactions carried out with branched carbon chains show very different results. This difference is mainly due to the role of α-C in linear aldehyde molecules. As seen previously, the linear aldehydes are much more prone to condensation reactions, leading to heavy product formation. In aldehydes with branched carbon chains, such as 2-ethyl-butanal and 2-methyl-pentanal, α-H is not readily accessible, making the reactions between two aldehyde molecules or an aldehyde and an alcohol molecule much more difficult. Therefore, these molecules do not readily participate in reactions that lead to the formation of heavy products, exhibiting a steric hindrance effect. Table 6 shows that no heavy products are produced from the reaction of 2-methyl-pentanal, except for small amounts of ether from the dehydration of 2-methyl-pentanol.

α,β-unsaturated aldehyde, which is the major primary by-product from aldol condensation of propanal, is a very active molecule and can further undergo various hydrogenation reactions [48]. Scheme 3 presents various hydrogen addition reactions that the 2-methyl-2-pentenal (D) molecule can undergo over $NiMoS/Al_2O_3$ catalysts. The hydrogenation of the C=O double bond (1, 2 addition) gives the unsaturated alcohol (T), which can further hydrogenate into the saturated alcohol (F). It can also undergo hydrogenolysis to form the corresponding unsaturated hydrocarbon (G). The 1,4-addition of hydrogen gives the enolic intermediate (U), which quickly isomerizes into saturated aldehyde (E) or further reacts with hydrogen to give unsaturated hydrocarbon molecules (V). The 3,4 addition of hydrogen can also give the saturated aldehyde (E) directly. Saturated aldehyde can further hydrogenate into saturated alcohol (F), as seen in Table 6. Saturated alcohols, in turn, can lead to saturated hydrocarbons (H), as seen in Table 7. All of the species represented in this scheme except the enolic intermediate (U) were observed in the propanal hydrogenation product stream over $NiMoS/Al_2O_3$ catalysts. These species were the primary products when 2-methyl-2-pentenal was used as the feed molecule (Table 8).

The second important group of side reactions in the propanal hydrogenation network (Scheme 1) involves those between aldehyde and alcohol species. These reactions can also lead to the formation of 2-methyl-pentanal (E) (Tables 5 and 12). An addition reaction between a propanal and a propanol molecule over an acidic site can lead to a hemiacetal intermediate (I). Hemiacetal, which is unstable, gives a propionaldehyde dipropyl acetal species (J) when reacted with another alcohol molecule. Propionaldehyde dipropyl acetal can undergo hydrocracking to give dipropyl ether (K) and propanol (Table 9). Dipropyl ether can further react to give propane (L) and propanol, as seen in Table 10.

Heavy products observed in the reaction product stream (M, N, O) are the results of additional condensation reactions involving C_6 aldehydes and alcohols further reacting with C_3 aldehydes.

While the evidence seen in our reaction studies and our TPD experiments clearly point to the role of the bare support in the catalysis of heavy product formation, it is not clear whether OH groups alone are responsible for these reactions. Studies in the literature have reported the activity of Al^{3+} sites in catalyzing condensation reactions of acetones [49,50]. It is known that the condensation of aldehydes can also be catalyzed by liquid [51] and solid [46,52] acid catalysts. Although the heavy product formation rates correlate very well with the density of surface OH groups, the contribution of other sites cannot be completely ruled out. The Brønsted acid sites associated with Mo centers can also be involved in condensation reactions, although their contribution is likely to be small. In our earlier papers, heavy product formation rates were seen to correlate with the CO_2 uptake capacity of the catalysts [37,38]. However, the fact that the heavy product formation rates do not extrapolate to the origin, even when CO_2 uptake is zero, may suggest the contribution of sites other than the OH groups to these reactions.

Other minor reactions involved in the aldehyde hydrogenation network (Scheme 1) in the presence of water include the reaction of propanal with water to give propionic acid (P). Further reaction with propanol may lead to ester formation (Q). Liquid-phase data obtained with and without water provide evidence of these reaction steps (Fig. 6).

Light products such as C_1–C_2 alkanes can be produced from the decarbonylation of propanal. Complete hydrogenation followed by cracking can also lead to the formation of small hydrocarbons. Light products account for only a very small percentage of the overall yield loss for these catalysts and show an increase with increasing Ni loading.

5. Conclusions

Propanal is shown to be a representative model compound for the study of the hydrogenation reaction of linear aldehydes. The main reaction in the aldehyde hydrogenation process is the hydrogenation of the C=O double bond, which takes place over the coordinatively unsaturated sites. The major side reactions are self-condensation of aldehydes and condensation of aldehydes with alcohols. Both reactions involve α-hydrogen and are primarily catalyzed by acid–base bifunctional sites over the exposed Al_2O_3 surfaces. In aldehyde molecules with a branched carbon chain, such as 2-ethyl-butanal and 2-methyl-pentanal, α-hydrogen is not readily accessible, making the condensation reactions much more difficult. The steric hindrance effect exhibited by branched-chain aldehydes is the main reason for the low heavy-product selectivities. The similarities between the trends observed in the gas phase and the liquid phase imply that the experimental results obtained in the gas phase are still relevant for industrial applications of similar reactions, which use primarily liquid feeds.

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