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Catalyzing the carbonylation of methanol using a heterogeneous vapor phase catalyst

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Abstract

Nickel supported on activated carbon has been shown to be active for the carbonylation of methanol. Methyl acetate was the major and primary product; acetic acid was formed as a minor product. The greatest yield of methyl acetate was approximately 0.21 at a reaction temperature of approximately 225°C. The effect of reduction temperature and nickel loading on the performance of catalyst is reported. The catalyst was mostly stable at temperatures near 225°C but deactivated irreversibly at elevated temperature. The results are consistent with a competitive reaction between the nickel catalyst and the activated carbon support, to produce an inactive nickel carbide product. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Current technology for acetic acid production relies on a multiphase reaction of methanol and CO, with an expensive rhodium catalyst dissolved in the liquid phase. The economic success of this process relies on the successful recovery and recycle of the catalyst, which can only be accomplished with great difficulty using a proprietary technology. This leads to the conclusion that a new technology for acetic acid manufacture using a heterogeneous catalyst based on a less expensive metal could provide greater economic incentive to produce this valuable commodity chemical.

The acetic acid process can be conveniently divided into two sections: synthesis and purification [1]. The synthesis reaction

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (1)$$

is carried out in the liquid phase in the presence of a homogeneous catalyst system containing the active catalyst and a promoter. Rhodium compounds are generally used as the catalyst for the process. The preferred promoter is methyl iodide. A commonly used solvent is a mixture of acetic acid and water.

For the homogeneous carbonylation of methanol over rhodium catalysts, the mechanism is well-known. The formation of a CH_3COI intermediate has been shown to be critical [2] leading to first-order dependence on methyl iodide concentration, as well as first-order dependence on the rhodium complex catalyst.

Although the production of acetic acid by low pressure carbonylation is commercially practiced, the process has several disadvantages. The use of the homogeneous reaction system requires a sophis-

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ticated separation section. The cost of the separation unit is approximately 110% of the cost of the reaction section. Successful recovery of the catalyst depends to a large extent on proprietary technologies [3]. The price of rhodium catalyst is relatively high. For example, in the Monsanto low pressure carbonylation process the cost of the catalyst is 5–10% of the total cost of the materials for the process [4].

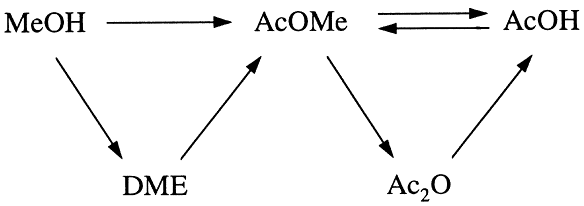
Several alternative processes and technological routes for acetic acid production have been considered. Generally, suggestions for alternative processes include a change to a low-cost heterogeneous catalyst, for example nickel, in the place of rhodium. Usage of a catalyst that is less expensive than rhodium decreases the capital cost for the reactor; immobilizing the catalyst simplifies the separation section by eliminating one distillation tower and decreases possible catalyst losses in the waste streams. Direct production from synthesis gas has also been proposed. Even if carried out in multiple processing steps, direct acetic acid production provides the opportunity for economic incentives resulting from improved process integration. Since coal-derived synthesis gas has the same H_2/CO ratio as acetic acid [5], direct production of acetic acid from coal-derived synthesis gas can be achieved with a minimum of undesirable byproducts. Recycling of produced water and heavy ends into the gasifier can be used to minimize the environmental impacts of the process.

Vapor phase carbonylation of methanol has been a subject of investigation for several years. The research has primarily focused on two possible catalysts for this reaction; rhodium supported on polymers or zeolites, and other metals supported on activated carbon.

In the study of Yashima et al. [6] rhodium chloride catalysts on different supports were considered. The study showed that the support plays an important role for the activity of the catalysts. The activity of Rh-Y zeolite catalyst was significantly higher than that for $RhCl_3/SiO_2$, $RhCl_3/Al_2O_3$, $RhCl_3/SiO_2–Al_2O_3$, and Rh cation exchange resin. Fujimoto et al. [7] compared various catalysts supported on activated carbon and reported that rhodium was the preferred catalyst, although nickel was also highly effective. The affinity of the halide ion with the metal was shown to be extremely important.

The influence of the supports was found to be very significant for the catalysts. It was discovered that activated carbon (AC) has unique properties for the reaction [7–10]. For example, Fujimoto et al. [7] reported that methanol carbonylation on Ni/γ-alumina catalyst yields primarily dimethyl ether, whereas reaction with Ni supported on activated carbon yields primarily acetic acid. It is reported that the activated carbon support suppresses hydrogen adsorption while promoting multiple CO adsorption [10], thereby leading to the high activity of this specific catalyst/support combination. It was also reported that Ni loading of approximately 5 wt% is preferred, since greater loading of nickel led to decreased dispersion and thus lower availability of surface sites.

Heterogeneous carbonylation of methanol is believed to proceed through a set of parallel and series reactions that produce methyl acetate and dimethylether as primary products, with acetic acid as the ultimate product, according to the reaction pathways described by Omata et al. [10] and reproduced as Eq. (2) below. The rate of this reaction was described by power law kinetics, but some adjustment of individual steps was required to match the experimental data.



(2)

Recent efforts have suggested activity enhancement from the addition of tin to the nickel on activated carbon catalyst (see e.g. Liu and Chiu [8]), although Sn/AC had little activity in its own right. They reported that tin improved both the activity of the catalyst and the selectivity to the methyl acetate product (relative to dimethylether); at low conversion, these researchers reported no acetic acid formation. However, substantial amounts of methane were reported in their experiments. It was postulated that one of the effects of tin addition was to enhance the quantity of CO adsorbed on the catalyst and increase the strength of the adsorption. In addition, a Ni_3Sn complex was observed, that could be active for the reaction.

Within the current paper, we describe our efforts to develop a heterogeneous catalyst comprised of nickel supported on activated carbon. Catalyst screening experiments that use a non-isothermal temperature profile have been completed to demonstrate that an active catalyst can be produced. Following a description of the experimental apparatus, the results are presented in terms of methyl acetate yield, identified as the major product in all cases.

2. Experimental

The reactor system is comprised of three sections: the feed train, the reactor assembly, and the analytical system, as shown in Fig. 1.

The feed train consists of a series of flowmeters to regulate the flow of reactant gases into the reactor. The feed gas is pure CO, provided from a commercially available gas cylinder (AGA Gas) and metered into the flow system through a two-stage regulator. For catalyst reduction, a gas mixture of N_2 and H_2 is produced from commercially available cylinders (AGA Gas) from separately metered feeds of the pure gases. The gases are mixed together and then fed through a pre-heater, made from a 150 ml sample cylinder wrapped with heating tape. The power to the heating tape is controlled with a temperature controller that maintains the gas pre-heat temperature to approximately 120°C. This temperature has been chosen so that the liquid feed species will easily vaporize into the gas stream, but it is not so high as to promote a thermal reaction between the feed components. A liquid metering pump (Cole-Parmer Masterflex pump with digital drive) is used to feed reactants that are normally liquids at room temperature – specifically methanol and methyl iodide. The liquid is then mixed with the gas feed in a 150 ml mixing vessel to ensure a well-mixed vapor stream.

All the feed species then proceed into the reactor, a quartz tube packed with catalyst powder. The reactor is surrounded by an aluminum heating block, which is wrapped with Cole-Parmer bead heaters; the temperature within the reactor is maintained by a temperature controller (Cole-Parmer ramp and soak controller) connected to a thermocouple located within the catalyst bed.

Following the reactor, the effluent gases pass into the analytical system. Provision is also made for sampling the inlet stream, as described in Fig. 1. All lines leading to the analytical system are heat traced to avoid condensation of reaction products. A Dycor 200M Residual Gas Analyzer (mass spectrometer) is used for quantitative analysis of the gas phase products. Because all the gaseous species have a different parent ion peak, continuous analysis through the mass spectrometer is possible without separation of the components.

Nickel catalysts supported on activated carbon have been produced using wet impregnation techniques. Commercially available Darco activated carbon (Aldrich Chemical) was used as the support in all

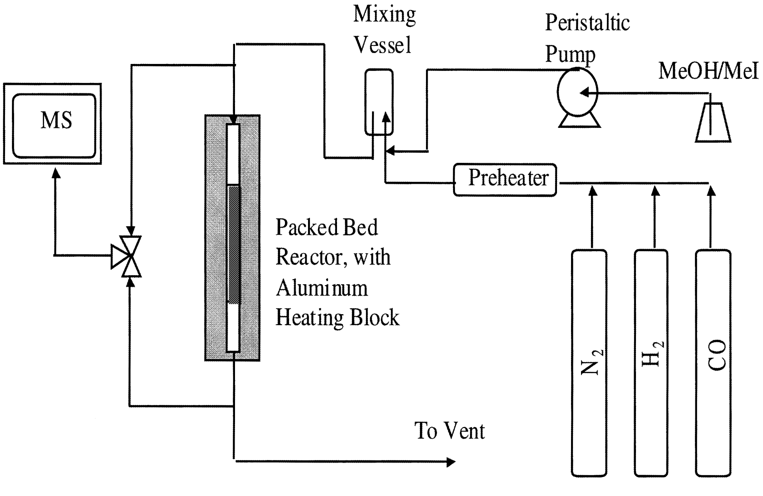


Fig. 1. Schematic diagram of experimental equipment.

cases. 20–40 mesh pellets were crushed to produce a powder with an average particle size of approximately 150 μm. Nickel, in the form of $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (commercially available, Aldrich Chemical) was weighed and dissolved into an organic solvent. Then, a measured amount of activated carbon was added to the vessel, to completely absorb all the liquid solution. The wet carbon was dried in a flowing nitrogen stream at 125°C, followed by overnight reduction in hydrogen (approximately 15 h).

Catalyst performance experiments have been accomplished using the packed bed reactor. Small samples of the catalyst (0.36–0.39 g) were placed into the reactor. Standard feed conditions, consisting of 17 mol% methanol, 82 mol% CO, and 1 mol% methyl iodide, were maintained during all these experiments. These conditions yielded $W/F=0.55\ g_{cat}$ h/mol, or a residence time of approximately 0.25–0.29 s.

Experiments were started at 150°C and run for 3–5 h, to allow the catalyst to reach a steady state. Following a steady state operation, a temperature programmed experiment was initiated. Reaction temperature was increased at a rate of 1°C/min up to about 280°C and then decreased to 200°C at the same rate. Conversion and product yield were monitored continuously, using the Dycor mass spectrometer, to obtain data in the form of conversion and yield as a function of temperature. The results are also compared with selected steady state experiments.

3. Results

Several catalysts have been prepared at the University of Toledo and tested according to the procedure described previously. Catalyst descriptions are provided in Table 1. In all cases, methyl acetate was observed as the major reaction product; small amounts of acetic acid were also observed. The results compare the performance of several catalyst formulations in terms of the yield of methyl acetate.

During the steady state portion of each experiment, the conversion of methanol and yield of methyl acetate were a function of the time on stream, as shown in Fig. 2 for Catalyst 4.3, a sample containing 6% nickel on activated carbon. Methanol conversion was initially greater than 0.30 and decreased to a steady value near 0.18. Methyl acetate yield increased steadily for 60 min, until a steady state yield of 0.025 was obtained. This was well below the level that would be expected from a carbon balance on the carbonylation reaction. Transitory high conversion of oxygenated organic species has previously been reported [11], owing to adsorption of the organic species on the catalyst surface without further reaction. The irreversible adsorption of oxygenated products may partially explain the low yield of acetic acid that is obtained, and the poor carbon balance observed during these experiments.

The temperature ramp reveals a peak yield of methyl acetate of approximately 0.05 at a temperature of approximately 220°C. As the temperature was increased further, the methyl acetate yield decreased, until essentially no methyl acetate was observed above 260°C. Methanol conversion was fairly constant at 0.15 until the temperature reached 220°C. Further increases in temperature led to a decrease in methanol conversion, with a conversion of 0.08 observed at 260°C.

Table 1
Summary of catalysts tested

Catalyst	Nickel loading (weight percent)	Reduction temperature (°C)	Comments
3.1	3	160	
3.2	3	180	
3.3	3	200	
4.0	0	—	
4.1	3.5	180	
4.2	6	180	Loaded in two steps, 3%, dried, then 3%, dried, reduced
4.3	6	180	Loaded in a single step
4.4	6	180	Loaded in two steps, 3%, dried and reduced, then 3%, dried and reduced
5.2	3.1	180	Reduced in situ

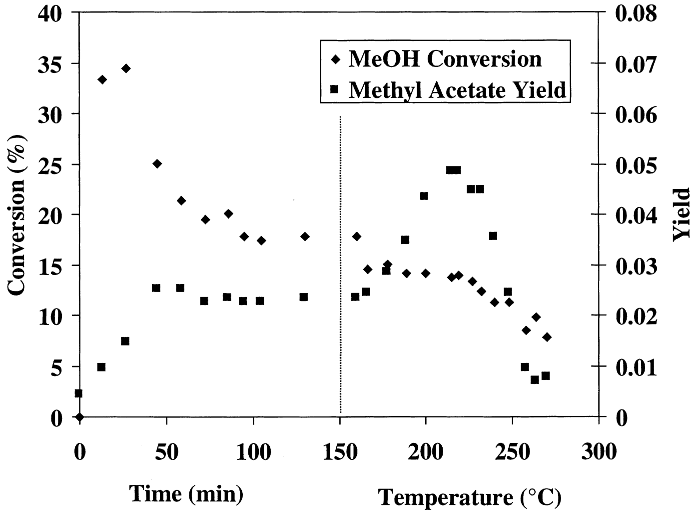


Fig. 2. Methyl acetate yield and methanol conversion during an experimental run, including steady state portion at 150°C and temperature ramp at 1°C/min. Catalyst 4.3.

Similar results are shown in more detail in Fig. 3, which reports results for catalyst 4.4, a catalyst sample produced with 6 wt% nickel in consecutive impregnation and reduction steps. In this case, a maximum methyl acetate yield of approximately 0.05 was observed at a temperature or approximately 225°C. Increasing the temperature above 250°C resulted in a methyl acetate yield that was less than 0.01. When the temperature was reduced back to 180°C and a second temperature ramp was performed, a maximum yield of methyl acetate of approximately 0.015 was observed near 225°C. These results reveal that a chemical change occurred on the catalyst during the high temperature portion of the ramp. Once the catalyst was deactivated, activity could not be restored through simple temperature reduction.

A similar result was observed from isothermal experiments, as indicated by the filled squares in Fig. 3. The first isothermal temperature was the point recorded at 225°C, for which the methyl acetate yield was approximately 0.05, almost identical to that recorded during the temperature ramp. Upon an increase in the temperature to 240°C, the catalyst began to show signs of deactivation, with a methyl acetate yield of approximately 0.03. This value was displaced from the value observed during the temperature ramp by approximately 5°C, perhaps indicating the effect of dead volume between the reactor and the mass spectrometer. A decrease in the temperature to 235°C led to a methyl acetate yield of approximately 0.015, comparable to that observed during the second temperature ramp.

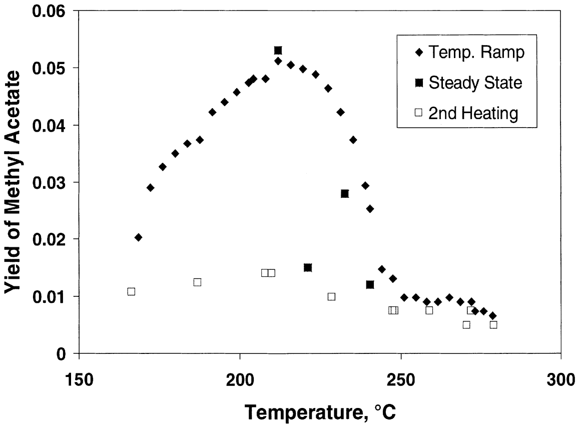


Fig. 3. Comparison of methyl acetate yield for two non-isothermal temperature ramps with the results obtained from steady state experiments. Catalyst 4.4.

Fig. 4 provides a comparison of catalyst performance (based on methyl acetate yield) for several catalysts prepared with differing amounts of nickel. The blank activated carbon revealed no activity for the carbonylation reaction. Three catalysts containing 6 wt% nickel were produced, one in a single nickel

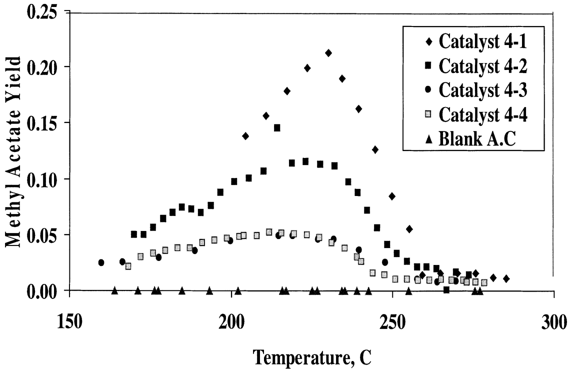


Fig. 4. The effect of nickel loading on catalyst performance.

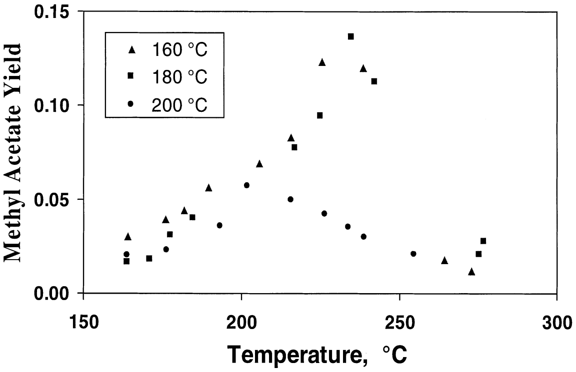


Fig. 5. The effect of reduction temperature on the performance of a catalyst containing 3% nickel.

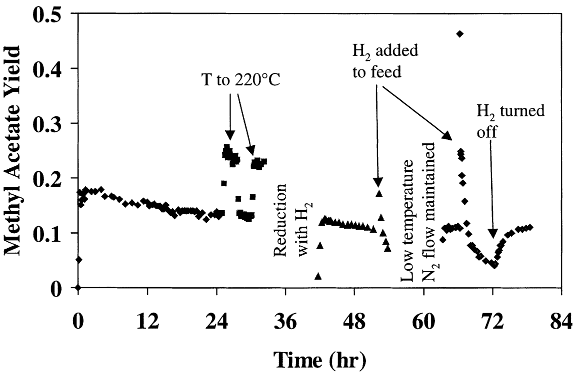


Fig. 6. Long term deactivation of catalyst 5.2. Reaction performed at 200°C, except for step changes as noted. Regeneration by flowing hydrogen at 200°C.

loading (Catalyst 4.3), one with an intermediate drying step (Catalyst 4.2), and one with an intermediate reduction step (Catalyst 4.4). All three catalyst samples containing 6 wt% nickel gave lower methyl acetate than the catalyst with 3.5% nickel loading. Of the 6% catalysts, the greatest methyl acetate yield was obtained from the catalyst with the intermediate drying step. The catalyst with the intermediate reduction gave a result that was identical to loading of nickel in a single step. Regardless of the nickel loading procedure, the catalyst was completely deactivated at a temperature slightly greater than 250°C and little yield of methyl acetate (or any other reaction products) was observed.

Finally, Fig. 5 reveals the effect of reduction temperature on the performance of the catalyst. These results are reported for catalyst 3, a series of catalysts produced with a nickel loading of approximately 3 wt%. For the two catalysts reduced at 160°C and 180°C, there was little effect of reduction temperature. Both catalysts gave a maximum methyl acetate yield of approximately 0.13 at 230°C. However, when the reduction temperature was increased to 200°C, the maximum methyl acetate yield was only 0.06 at approximately 200°C. All three catalysts were deactivated and had essentially no activity above about 260°C, and no activity could be recovered from any of these catalysts during a second temperature ramp.

In the previous discussion of Fig. 2, we noted that the methyl acetate yield was well below the value that should be obtained on the basis of a carbon balance. This result was attributed to the possible irreversible adsorption of oxygenated organic compounds, and in particular, the adsorption of acetic acid. In order to test this hypothesis, an extended run (approximately four days) was conducted at 200°C. During this time, the methyl acetate yield decreased steadily from a high of approximately 0.2 to a steady state value of 0.1, as shown in Fig. 6. At the beginning of the run, there was a transient period during which the yield of methyl acetate rapidly increased to a "steady" value. After 24 h at 200°C, an increase of reaction temperature to 220°C increased the methyl acetate yield to approximately 0.25. Upon returning to 200°C, the methyl acetate yield returned to its previous value and the catalyst resumed its deactivation.

Reduction with hydrogen also did not restore the catalyst activity. After reduction for 10 h at 200°C, methyl acetate increased to the previous value through an initial transient response, after which time the deactivation continued along the same trendline as had been observed prior to reduction. However, when hydrogen was added to the feed, a large transient yield of methyl acetate was observed. Continued addition of hydrogen gave a stable methyl acetate yield below that expected from the deactivation curve. Methyl acetate yield returned to the expected value after hydrogen feed was stopped.

Only limited characterization of the catalyst samples has been performed at this time. Surface area measurements have been obtained through the use of a Quantisorb nitrogen adsorption device. Fresh activated carbon had a surface area of 1192 m^2/g and prepared catalyst (sample 4.4) containing 6 wt% nickel had a surface area of 876 m^2/g. Following the temperature programmed reactions, the catalyst surface area was found to be 788 m^2/g, a small change relative to that obtained for the fresh catalyst.

4. Discussion

The nickel on activated carbon catalyst has been effective in promoting the carbonylation of methanol to yield methyl acetate as a major product. However, reaction temperatures in excess of 230°C lead to rapid deactivation of the catalyst. It has been suggested that this loss of activity may be due to a number of possible phenomena (Engineering Foundation Conference: Reactor Engineering for Sustainable Development, Banff, Canada, June 1997). However, specific experimental evidence discounts some of these theories.

The methyl acetate may be produced through reaction of adsorbed nickel acetate and gas phase methanol. After the nickel acetate is depleted, catalyst activity ceases, explaining the deactivation at higher temperatures. However, comparison of the amount of nickel acetate adsorbed onto the catalyst with the amount of methyl acetate produced reveals that there is insufficient acetate ion in the original catalyst formulation. In addition, the low temperature steady state experiments were run for different amounts of time for each catalyst sample, whereas the maximum yield was generally observed at the same temperature (225°C). Since the rate of depletion of adsorbed acetate would be dependent upon reaction time and initial loading, the identification of a consistent optimum temperature would be an extreme coincidence, if this postulate was correct.

A second consideration is the reaction of nickel with carbon monoxide in the reactor feed, leading to the production of nickel carbonyl. This product is highly volatile and extremely toxic, so would be important if it were produced. However, we have monitored for the production of nickel carbonyl using the mass spectrometer and have observed this product in only the case where CO was fed to the reactor as a pure species. The nickel carbonyl was detected both through the mass spectrometer and by the formation of a metallic film on the surface of the reactor tube. Thus, we consider the formation of nickel carbonyl during the reaction as unlikely.

The deactivation noted in Fig. 6 is consistent with adsorption of reaction products. The products were apparently stripped by the addition of hydrogen, however, hydrogen apparently competes with methanol for the active sites, inhibiting the desired carbonylation reaction. Although deactivation by adsorption was observed, this was a slow process occurring over several days and cannot be used to explain the rapid deactivation observed as the temperature was increased above 230°C.

One final possibility for the high temperature deactivation observerd during the temperature ramp experiments is that nickel reacts with carbon to form nickel carbide. Although no specific tests of the used catalyst have been performed to confirm this hypothesis, the proposed mechanism is consistent with the experimental results. Nickel carbide formation would lead to deactivation through two mechanisms: (1) the nickel metal is reduced to an inactive form, and (2) the inactive nickel carbide blocks the catalyst pores decreasing the accessibility to active nickel sites.

Careful examination of Figs. 4 and 5 provides indirect experimental evidence. Fig. 5 compares the effect of reduction temperature. As the reduction temperature is increased, the rate of the formation reaction for nickel carbide is also increased. This provides lower initial activity with increasing temperature, as observed. Since the catalyst reduced at 200°C already contains substantial quantity of nickel carbide, it deactivates faster, and the optimum yield of methyl acetate is never observed.

The effect of nickel loading reported in Fig. 4 is also consistent with the formation of nickel carbide.

As the nickel concentration is increased from 3.5% to 6%, the rate of the reaction should increase (assuming positive order kinetics in nickel, as would be expected at low concentrations). However, the higher nickel loading leads to higher yield of nickel carbide and greater blockage of the catalyst pores, decreasing the amount of accessible catalytic sites. As a result, 6 wt% catalyst is more highly deactivated under all conditions and lower yields are observed. The catalyst produced with two reduction steps is even more greatly enriched with nickel carbide, and has a still lower activity, as observed.

Although not confirmed through direct evidence, the experimental results are consistent with deactivation through reaction of the nickel catalyst with the activated carbon support. The formation of nickel carbide, if occurring, results in a material that has no activity for the carbonylation reaction. Further characterization of the used catalyst is currently underway to confirm the formation of nickel carbide.

5. Summary

Nickel on activated carbon has been shown to be an active catalyst for the formation of methyl acetate through the carbonylation of methanol. The greatest yield of methyl acetate was obtained for a catalyst containing 3.5 wt% nickel and reduced at 180°C at a reaction temperature of approximately 225°C. Reduction at a higher temperature or higher loads of nickel led to a catalyst that was less active for the carbonylation reaction. Results obtained from a temperature ramp of 1°C closely matched those obtained from isothermal experiments. Rapid deactivation of the catalyst occurs at elevated temperatures, possibly through a competitive reaction between the nickel catalyst and the activated carbon support. A slow deactivation also occurs, probably through irreversible adsorption of reaction products. Further examination of the used catalyst should confirm whether the formation of nickel carbide would be a major limitation to the development of this catalyst for carbonylation of methanol.

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