



Selective hydrogenation of acetone to methyl isobutyl ketone (MIBK) over co-precipitated Ni/Al₂O₃ catalysts

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Abstract

Ni/Al₂O₃ catalysts have been prepared by the co-precipitation method and have been studied for acetone hydrogenation at atmospheric pressure in the temperature region 373–473 K. Effects of metal content, reaction temperature and flow rate of the feed on the conversion and product selectivity are reported. It is possible to selectively synthesize methyl isobutyl ketone (MIBK) or 2-propanol by varying experimental conditions. More than 95% selectivity towards MIBK is reported on 10 wt.-% Ni/Al₂O₃ catalyst at 373 K and at 1 atmosphere.

Keywords: Ni/Al₂O₃; Acetone hydrogenation; 2-Propanol; MIBK

1. Introduction

Acetone hydrogenation is an important reaction with respect to its application in chemical heat pump for waste heat recovery for which a high selectivity to 2-propanol is required. The reaction is usually carried out at atmospheric pressure in the temperature region 423–523 K. Another interesting product of this reaction is methyl isobutyl ketone (MIBK) which is a valuable chemical. MIBK is mainly used as a solvent for cellulose and resin based coating systems and also for vinyl, epoxy and acrylic resins. The commercial production of MIBK involves a three step process [1,2]: (i) acetone is first converted to diacetone alcohol (DAA) by aldol condensation of acetone, (ii) dehydration of DAA to mesityl oxide (MSO), and (iii) selective hydrogenation of MSO to MIBK. Methyl isobutyl ketone can also be prepared by hydrogenation of

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acetone in a single step [3]. Catalytic conversion of acetone to MIBK in one step has been reported over several supported Pd catalyst systems [4]. High selectivity to MIBK (> 90%) is reported in the temperature region 353–433 K with an overall acetone conversion of nearly 40%. However, the operating pressure is between 10 and 100 atmosphere which may be a disadvantage. Supported nickel catalysts [1,2,5–7] have been used for acetone hydrogenation reactions by several workers. Gandia and Montes [1] report a highly selective one-step formation of MIBK from acetone with a magnesia supported nickel catalyst at atmospheric pressure and at 473 K. They have also studied the effect of reduction temperature on the selectivity of products for this reaction over Al_2O_3 and TiO_2 supported nickel and cobalt catalysts [5]. Very often, the supported metal catalyst systems give 2-propanol as the main reaction product. Effort on the investigation of the supported catalyst system is still required as a part of the exercise to develop a catalytic system for the production of the valuable MIBK by the hydrogenation of acetone especially at low temperature and at atmospheric pressure. We have been working on the preparation, modification and dispersion studies of supported nickel systems [8–13]. In this communication, we report the vapour phase hydrogenation of acetone over co-precipitated $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts and explore the possibility of using such catalysts at low temperature (373 K) and at atmospheric pressure to produce MIBK.

2. Experimental

$\text{Ni}/\text{Al}_2\text{O}_3$ catalysts with varying percentages of Ni (10–50 wt.-%) were prepared by co-precipitation following the procedure described by us earlier [8]. The catalysts thus prepared by constant and varying pH methods were all washed, dried and then calcined in air at 723 K for 12 h. After calcination, they were reduced in flowing H_2 at 723 K for 24 h and were then passivated in an air– N_2 mixture. The catalyst was also modified with a small amount of additives such as Mg, Fe and Co. Additives were added either during precipitation (Fe and Co) or after precipitation (impregnation of Mg).

Surface area of the catalysts were measured by N_2 adsorption at 77 K using a Micromeritics Pulse Chemisorption Unit (Model 2700). Hydrogen and oxygen adsorption measurements at room temperature and 673 K respectively were carried out in a high vacuum apparatus following the usual procedure [9]. Metal area and percentage reduction of the catalysts were calculated from the H_2 and O_2 adsorption measurements [9] and have been reported already [8].

2.1. Catalysis

Ca. 500 mg of catalyst particles (20–30 mesh) was loaded in a vertical glass tubular reactor of I.D. 10 mm and kept in place between layers of glass beads

and glass wool. Acetone was fed from the top of the reactor with the help of a motorised syringe at a controlled rate. H_2 was also fed from the top at a specific flow rate ($80 \text{ cm}^3 \text{ min}^{-1}$). Acetone hydrogenation was carried out in the temperature region 373–473 K at atmospheric pressure. The liquid products were collected in an ice trap and were analysed using a gas chromatograph with a s.s. column ($1/8'' \times 8'$) of 5% Carbowax 20 M on Chromosorb W in a temperature programmed mode from 323–373 K ($10^\circ\text{C min}^{-1}$). The main products of the reaction identified were 2-propanol and MIBK. Under severe reaction conditions, traces of acetyl acetone (AA), diacetone alcohol (DAA) and some isophorone were found.

3. Results and discussion

In Table 1, the conversion and selectivities of products of acetone hydrogenation over supported nickel catalysts containing 10 wt.-% Ni are given. The results obtained using Mg, Fe and Co modified catalysts are also given for comparison. It must be emphasized that the reaction was carried out at temperatures as low as 373 K. 10 wt.-% Ni/ Al_2O_3 catalyst prepared by precipitation at varying pH condition gave acetone conversion of 36% with nearly 96% MIBK selectivity. It is surprising, however, that Ni/ Al_2O_3 prepared by precipitation at constant pH yielded acetone conversion of 54% with MIBK selectivity of only 29%; the balance being 2-propanol. Except for the BET area, there is no significant difference in hydrogen uptake, metal area and percentage reduction between the catalysts A and B [8]. However, addition of Mg by impregnation and Fe and Co during precipitation to Ni/ Al_2O_3 catalyst (constant pH) improved the selectivity of MIBK to 90–97%; though the acetone conversion is reduced to around 38–47%. Catalysts with low surface areas (A, C, D and E) show high selectivity for MIBK when compared with catalyst having relatively higher surface area (catalyst B). The reduced surface area probably help in the easy desorption of MIBK into the gas phase as soon as it is formed, thus leading to its high selectivity on them [5].

Table 1
Acetone hydrogenation over 10 wt.-% Ni/ Al_2O_3 catalysts at 373 K

Catalyst	Precipitation conditions	Additives	BET area ($\text{m}^2 \text{ g}^{-1} \text{ cat}$)	Acetone conversion (%)	Selectivity (%)		
					2-propanol	MIBK	Acetyl acetone
A	varying pH	–	197	36	4	96	–
B	constant pH	–	290	54	71	29	–
C	constant pH	1.8% Mg	230	38	–	92	8
D	constant pH	1% Fe	202	47	–	94	6
E	constant pH	1% Co	225	43	–	97	3

Feed rate of acetone = $9 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1} \text{ cat}$.

Table 2

Effect of Ni loading on acetone hydrogenation over Ni/Al₂O₃ (varying pH) at 373 K

Ni loading (wt.-%)	BET area (m ² g ⁻¹ cat)	Acetone conversion (%)	Selectivity (%)	
			2-propanol	MIBK
10	197	36	4	96
20	168	48	53	47
30	166	72	100	–
40	164	80	100	–
50	160	90	100	–

In Table 2, the effect of nickel loading on acetone conversion and product selectivities are shown. With increasing nickel loading from 10–50 wt.-%, acetone conversion increases from 36–90%. Metal loading favours 2-propanol formation at the cost of MIBK. Irrespective of the method of preparation of nickel catalysts, whether the precipitation is made at varying or constant pH conditions, high metal loading is favourable to 2-propanol formation.

Effect of temperature on the reaction is shown in Table 3 using a 10 wt.-% Ni/Al₂O₃ catalyst (varying pH). With the increase in temperature from 373–473 K, the conversion increases from 36–71%. Nevertheless, MIBK selectivity decreases with the formation of other products such as acetyl acetone (AA). The increase of temperature does not seem to favour 2-propanol formation. The feed rate effect on the conversion and selectivities is shown in Table 4. As expected, the conversion decreases with the feed rate and at lower conversion, the selectivity towards MIBK increases. For example, at 42% conversion (F.R. = 9 cm³ h⁻¹ g⁻¹ cat), MIBK selectivity is only 87% where as at 21% conversion (F.R. = 18 cm³ h⁻¹ g⁻¹ cat), MIBK selectivity has gone up to nearly 100%.

Analysis of these results, though of preliminary nature, reveal an interesting observation viz., it is possible to hydrogenate acetone under vapour phase conditions to get selectively MIBK at temperature as low as 373 K and at atmospheric pressure. It is, of course, possible to selectively synthesize 2-propanol from acetone hydrogenation over Ni/Al₂O₃ catalysts.

To the best of our knowledge, the selective formation of MIBK upto 97% in the conversion level of 36–47%, especially at 373 K and atmospheric pressure,

Table 3

Temperature effect on acetone hydrogenation over 10 wt.-% Ni/Al₂O₃ (varying pH)

Temperature (K)	Acetone conversion (%)	Selectivity (%)		
		2-propanol	MIBK	Acetyl acetone
373	36	4	96	–
423	42	3	87	10
473	71	3	66	29

Feed rate of acetone = 9 cm³ h⁻¹ g⁻¹ cat.

Table 4
Effect of feed rate on acetone hydrogenation over 10 wt.-% Ni/Al₂O₃ (varying pH) at 423 K

Feed rate of acetone (cm ³ h ⁻¹ g ⁻¹ cat)	Acetone conversion (%)	Selectivity (%)		
		2-propanol	MIBK	Acetyl acetone
9	42	3	87	10
12	37	–	93	7
18	21	–	100	–

has not been reported so far. The fact that low wt.-% nickel (10 wt.-%) favours MIBK and high wt.-% nickel (> 10 wt.-%) favours 2-propanol formation indicate the differences in the mechanism of acetone hydrogenation yielding different products. A simple hydrogenation of > C=O group in the presence of active metal sites may yield only 2-propanol. However, the formation of MIBK may require both metal as well as the acid–base sites of the support. The mechanism of the reaction has been explained by Gandia and Montes [5]. One possibility of formation is by the three-step process: acetone → DAA → MSO → MIBK. Another possibility is the formation of 2-propanol in the first step by simple hydrogenation followed by the condensation of 2-propanol and acetone to give MIBK. However, at present, we do not have enough evidence to back up the second possible mechanism since the experiments involving hydrogenation of acetone and 2-propanol mixture over the catalysts in the same temperature region did not yield the expected MIBK.

4. Conclusion

10 wt.-% Ni/Al₂O₃ catalysts prepared by co-precipitation is highly selective to MIBK formation in the vapour phase hydrogenation of acetone at 373 K and at atmospheric pressure. Selective formation of 2-propanol is possible at higher metal content. Additives such as Mg, Fe and Co-oxides help to improve MIBK selectivity. The pH conditions during precipitation of catalysts containing low metal content seem to affect acetone hydrogenation.

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