Cation-exchanged montmorillonite catalyzed hydration of styrene derivatives

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Abstract

Iron-exchanged Wyoming montmorillonite (Fe^{3+}-SWy-1) is quite an effective catalyst for the hydration of styrene derivatives. The yields and selectivities depend on the reaction conditions, with good efficiency attained using THF as solvent at 120°C. Fe^{3+}-SWy-1 calcined at 300°C, and pillared clays (PIL.Fe^{3+}-SWy-1), either air dried or calcined at 300°C, were inactive for the hydration of styrene. The hydration of styrene was also investigated in the presence of a cation-exchanged Fluka K10 montmorillonite (M^{n+}-K10). Fe^{3+}-K10 was found to be the most effective catalyst. However, it shows less activity, selectivity and reproducibility than Fe^{3+}-SWy-1. © 1997 Elsevier Science B.V.

1. Introduction

The hydration of olefins is one of the most important processes for the production of alcohols [1]. Homogeneous methods based on sulfuric acid and heteropolyacids, although affording products in high yields, suffer from several disadvantages including corrosion of the equipment, difficulty of product separation, necessity to concentrate the acid for reuse and waste disposal.

Transition metal complexes have been investigated as catalysts for the hydration of electron deficient olefins. Vinyl fluoride and 1,1-difluoroethylene were hydrated using

chlororuthenate(II) species as catalysts [2]. Malic acid was prepared by the hydration of maleic acid in the presence of various aluminum and chromium chloride [3]. Hydration of diethyl maleate to diethyl malate catalyzed by divalent complexes of palladium(II) has been studied in aqueous THF [4,5]. *Trans*-PtHCl(PMe_3)_2 was claimed to catalyze hydration of 1-hexene to 1-hexanol in the presence of aqueous NaOH and benzyltrimethylammonium chloride at 60°C [6,7]. Unfortunately, attempts to effect the claimed catalysis was unsuccessful [8]. Recently, the Pt–OH bond of *cis*-Pt(OH)(Me)(PPh_3)_2 was shown to undergo syn addition of the C=C bond of dimethyl maleate to give *cis*-PtMe{CH(CO_2Me)CH(OH)-CO_2Me}(PPh_3)_2 [9,10]. Treatment of this Pt–C σ-bonded complex with aqueous acids gave

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$[PtMe(H_2O)(PPh_3)_2]^+$ and dimethyl malate. Enzymes can also catalyze the hydration of olefins. Fumarase and aconitase, respectively, catalyze the hydration of fumarate to L-malate and aconitate to isocitrate or citrate [11].

Cation-exchanged montmorillonites have been investigated as heterogeneous catalysts in a wide range of organic reactions [12–17]. To our knowledge, there are no reports on the hydration of styrene derivatives using clays as catalysts. However, the synthesis of alcohols from C_2–C_6 aliphatic olefins catalyzed by ion-exchanged montmorillonites has been described. Several ion-exchanged montmorillonites (H^+, Al^{3+}, Fe^{3+} and Cr^{3+}) were examined for ethylene hydration, [18] with Al^{3+}-montmorillonite as the most active catalyst leading to 5% conversion (based on water) per pass. A variety of acid-treated clays were also tested for the hydration of ethylene and propene [19–24]. The use of Cr^{3+}-montmorillonite as a catalyst for the hydration of C_3–C_4 olefins such as propene, 2-methylpropene, 1-butene, and 2-butene was claimed to be twice as active as non-exchanged montmorillonite [25]. Branched-chain C_6 alkenes yielded alcohols below 40°C, in the presence of Cu^{2+}-montmorillonite [26]. We report herein the hydration of styrene derivatives catalyzed by cation-exchanged K10 montmorillonite (M^{n+}-K10) and Wyoming montmorillonite (M^{n+}-SWy-1).

2. Experimental

2.1. Materials

K10-montmorillonite was obtained from Fluka. SWy-1-montmorillonite was received as crude material from the source clays repository, University of Missouri. All styrene derivatives were purchased from Aldrich Chemical and used without further purification.

Na^+-K10 and H^+-K10 were prepared as described previously, except that the catalysts were air-dried [13]. M^{n+}-K10 was prepared by treatment of Na^+-K10 with the corresponding salts solutions.

Solvents were dried and distilled prior to use by known methods.

2.1.1. Preparation of Na^+-SWy-1

Crude SWy-1-montmorillonite was purified so as to be free of all quartz, calcite and dolomite impurities by mechanical dispersion in distilled water (1 g of clay/100 ml of water), followed by acid and base treatment. The < 2 μm size fraction was siphoned off from the bottom sediment and treated several times with a 1 M NaCl solution. It was then dialyzed in dialysis bags for a week until the dialyzate did not react with $AgNO_3$. The Na^+-exchanged montmorillonite so obtained was freeze-dried and designated as Na^+-SWy-1.

2.1.2. Preparation of Fe^{3+}-SWy-1

A weighed amount of solid $Fe(NO_3)_3.9H_2O$ was dissolved, at 23°C, in 100 ml of distilled water to give 1 M of a clear reddish brown solution (pH = 1.7). 100 ml of this freshly prepared solution was added dropwise to a vigorously stirred solution of 1 g of Na^+-SWy-1 dispersed in 15 ml of distilled water at 50°C for 24 h. The pH of the resulting slurry was 1.8. The exchange was completed by adding 200 ml of cold distilled water to the reaction medium and the resulting solution was poured in a 250 ml teflon centrifuge bottle. Centrifugation and washing with distilled water (250 ml) were alternated until a nitrate free and clear supernatant was obtained. The exchanged clay was dried overnight at 70°C, was ground and passed through a 250 mesh screen.

2.1.3. Preparation of $PIL.Fe^{3+}$-SWy-1

In the pillaring procedure, to the freshly prepared ferric nitrate 1 M solution, an exact volume of 2 M NaOH was added dropwise and under vigorous magnetic stirring, in order to obtain a molar ratio of OH/Fe = 2. A red dark

Table 1
Characteristics of Na^+-SWy-1, Fe^{3+}-SWy-1 and PIL.Fe^{3+}-SWy-1

Entry	Catalyst	% Na	% Fe_T [a]	% Fe_E [b]	%Fe_P [c]	Basal spacing (Å)
1 [d]	Na^+-SWy-1	0.098	2.3	—	—	12.5
2 [e]	Na^+-SWy-1	0.098	2.3	—	—	9.7
3 [d]	Fe^{3+}-SWy-1	0	3.53	1.23	—	14.3
4 [e]	Fe^{3+}-SWy-1	0	3.53	1.23	—	9.7
5 [d]	PIL.Fe^{3+}-SWy-1	0	12	—	9.7	21.6
6 [e]	PIL.Fe^{3+}-SWy-1	0	12	—	9.7	14.7

[a] Ratio by weight of the total amount of iron present in the sample.
[b] Ratio by weight of the amount of iron inserted by exchange reaction.
[c] Ratio by weight of the amount of iron inserted by pillaring reaction.
[d] The sample was air dried.
[e] The sample was calcined at 300°C.

solution of pH = 1.7, free of any precipitate, was obtained, and was aged for 24 h at room temperature. It was then filtered (Whatman, qualitative filter paper No. 5) to afford a clear solution, 100 ml of which was added dropwise under vigorous stirring to the dispersed Na^+-SWy-1 in 15 ml of distilled water at 50°C for 5 h. The pH of the resulting slurry was 1.8. Pillaring was completed by adding 200 ml of cold distilled water to the reaction medium and the resulting solution was poured in a 250 ml teflon centrifuge bottle. Centrifugation and washing with distilled water (250 ml) were alternated until a nitrate free and clear supernatant was obtained and the pillared clay was dried overnight at 70°C. The resulting pillared clay was ground and passed through a 250 mesh screen.

The characteristics of Na^+-SWy-1, Fe^{3+}-SWy-1 and PIL.Fe^{3+}-SWy-1 are presented in Table 1.

2.2. Instruments

The products were identified by gas chromatography (Hewlett 5890, Packard Series II), using a 10 ft column with 1.5% OV-17 and 1.95% OV-210 as the stationary phase. t-butylbenzene was used as a calibration standard. ^{1}H NMR spectral determinations were made on a Varian Gemini 200 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard.

A Philips PW3710 X-ray diffractometer (Ni-filtered CuK α radiation) was used to ensure the effectiveness of the purification of all the materials and in particular the absence of any iron hydroxide/oxide phases, and to determine their basal spacing.

Samples for XRD measurements were prepared by allowing an ultrasonic dispersion of 40 mg of the clay in 2 ml of distilled water to air dry on a glass slide. XRD patterns were recorded at 45 kV and 40 mA, by step type scanning with a step size of 0.02 [°2θ] at $1/2$° 2θ/mn between the interval 3° to 90° (2θ).

The metal content of the catalysts was obtained by atomic absorption spectroscopy (AAS), using a Varian Spectr. Plus 250. 10 mg of each sample was dissolved in a nalgene container with 10% ml HCl (50 ml) and 49% HF (2 ml) at 60°C overnight. The iron content was analyzed by absorption with a 25 mA lamp and the sodium was analyzed by emission.

2.3. Catalytic hydration procedure

In a 45 ml autoclave equipped with a glass liner, containing a stirring bar and 2 ml of solvent, was placed the catalyst (0–500 mg) and water (0–14 mmol). To this mixture was added a solution of the styrene derivative (1–10 mmol). The autoclave was purged with nitrogen, and then heated to the desired temperature for the required reaction time. The autoclave was then cooled to room temperature, the reaction mixture was filtered, and the filtrate was dried ($MgSO_4$), and evaporated. The crude mixture was analyzed by gas chromatography. The isolated yields were determined after purification of the products by flash-chromatography using pentane followed by pentane/ethyl acetate (9/1) as eluant.

3. Results and discussions

3.1. Hydration of styrene using M^{n+}-K10

When styrene was allowed to react with water in THF at 120°C, in the presence of 0.5 g of Fluka K10 montmorillonite, α-methylbenzyl alcohol was obtained in trace amounts (Table 2, entry 1). No reaction occurred when Li^+-K10 was used as the catalyst, while Zn^{2+}- and Cu^{2+}-K10 proved ineffective leading only to polystyrene (Table 2, entries 2–4). Under the same conditions, different M^{n+}-K10 were examined (Table 2, entries 5–11). In terms of both the activity and selectivity, the highest efficiency was obtained with Fe^{3+}-K10. Mercury(II)- and Ru^{3+}-K10 gave low selectivities, with ethylbenzene and acetophenone as the major by-products. Acid-treated montmorillonite (H^+-K10) gave 2% yield with only 12% selectivity, leading principally to polystyrene and high boiling point products (Table 2, entry 11). When the amount of Fe^{3+}-K10 was reduced to 50 mg, attempts to get reproducible activity was unsuccessful. This fact, in addition to the preparation of commercial K10-montmorillonite by acid attack on the clay, prompted us to use wyoming clay which is not pre-treated with an acid.

Table 2
Hydration of styrene using M^{n+}-K10 [a]

Entry	M^{n+}-K10 (M^{n+}, mmol)	Time (h)	Yield (%)	Selectivity (%)
1	K10	44	traces	—
2	Li^+-K10 [c]	44	0	—
3 [b]	Zn^{2+}-K10 [c]	44	0	—
4 [b]	Cu^{2+}-K10 (0.16)	44	traces	—
5	Zr^{4+}-K10 (0.38)	44	3	61
6	Co^{2+}-K10 (0.16)	43	5	70
7	Hg^{2+}-K10 (0.04)	48	6	52
8	Fe^{3+}-K10 (0.16)	44	7	82
9	Ru^{3+}-K10 (0.11)	44	6	30
10	Fe^{2+}-K10 (0.13)	44	6	62
11	H^+-K10	44	2	12

[a] Conditions: styrene (1 mmol) was reacted with water (10 to 14 mmol) in THF at 120°C in the presence of 0.5 g of clay in a 45 ml autoclave.
[b] polystyrene was obtained.
[c] The metal content was not determined.

Table 3
Hydration of styrene using Fe^{3+}-SWy-1 [a]

Entry	Catalyst	Solvent	T^{re} (°C)	Yield (%)	Selectivity (%)	TON
1	Na^+-SWy-1	THF	120	0	—	0
2 [b]	$FeCl_3$	THF	120	0	—	0
3 [c]	Fe^{3+}-SWy-1	THF	120	7	92	< 1
4	Fe^{3+}-SWy-1	THF	120	7	95	7
5 [d]	Fe^{3+}-SWy-1	THF	120	traces	—	—
6 [e]	Fe^{3+}-SWy-1	THF	120	6	90	6
7	Fe^{3+}-SWy-1	THF	180	1	29	1
8	Fe^{3+}-SWy-1	DME	120	5	85	5
9	Fe^{3+}-SWy-1	DMSO	120	0	—	0
10	Fe^{3+}-SWy-1	DMF	120	0	—	0
11	Fe^{3+}-SWy-1	PhH	120	0	—	0

[a] Conditions: 1 mmol of styrene was reacted with water (10 to 14 mmol) in a 45 ml autoclave in the presence of 50 mg of Fe^{3+}-SWy-1 for 48 h.
[b] 0.01 mmol of $FeCl_3$ was used.
[c] 500 mg of Fe^{3+}-SWy-1 was used.
[d] No water was used.
[e] Fe^{3+}-SWy-1 was recovered from entry 4 and reused without any pretreatment.

3.2. Hydration of styrene derivatives using M^{n+}-SWy-1

No reaction occurred when styrene was treated with water in THF at 120°C for 48 h in the presence of Na^+ exchanged-Wyoming montmorillonite (Na^+-SWy-1) or $FeCl_3$ (Table 3, entries 1 and 2). When the reaction was conducted with 500 mg of Fe^{3+}-SWy-1 (Fe^{3+} content = 1.23 wt%), obtained by treating sodium exchanged-montmorillonite with 1M $Fe(NO_3)_3$, α-methylbenzyl alcohol was obtained in 7% isolated yield and 92% selectivity (Table 3, entry 3). Under the same conditions, hydration reactions of styrene were conducted with different amounts of Fe^{3+}-SWy-1 The results shown in Fig. 1 indicate that the optimum amount of catalyst required is 50 mg. However, the selectivities remained unchanged. In the absence of water only traces of alcohol were detected (Table 3, entry 5). These interesting results indicate that the reaction takes place in the interlamellar region of the clay, that the reaction is catalyzed by intercalated Fe^{3+}, and that when the original interlamellar water, strongly polarized by coordination to the cations,
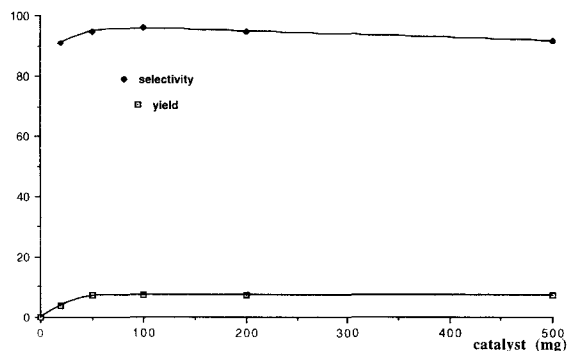
Fig. 1. Hydration of styrene (1 mmol) with water (10 to 14 mmol) catalyzed by different amounts of Fe^{3+}-SWy-1 in THF at 120°C for 48 h.

has been consumed, the catalyst life was extended by added water. The Fe^{3+}-SWy-1 was found to be effective even upon reuse (Table 3, entry 6). As shown in Table 3, the hydration of styrene depends on the reaction temperature and the nature of the solvent. In the case of THF, increase of the reaction temperature from 120 to 180°C leads to the expected alcohol in only 1% yield and 29% selectivity (Table 3, entry 7). This low reactivity is probably due to the collapse of the catalyst interlayers. The use of DME as the solvent leads to almost the same result as THF while no alcohol was detected when DMSO, DMF or PhH were used as solvents. In the case of DMSO and DMF, this is probably due to the coordination of solvent molecules to the interlayer cations resulting in the lack of access of the reactant molecules to the highly polarizing region near the interlayer
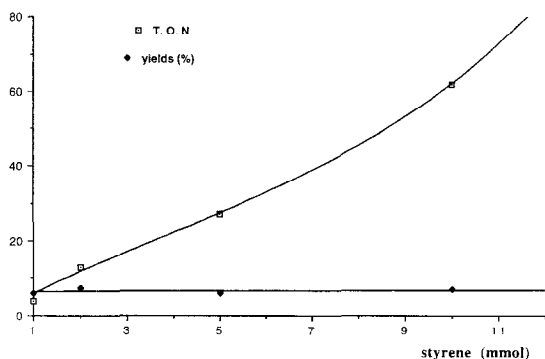
cation. In the case of benzene, the lack of miscibility with water is probably the main factor. Thus, the best results obtained in THF can be explained by the capacity of this solvent to provide miscibility and diffusion of both styrene and water to the interlamellar region of the clay. Fig. 2 shows that the turnover number (TON) increases as more styrene is used for the reaction but the yield seems to be independent of this factor. These results indicate that there is an equilibrium between the starting olefin and the alcohol. Indeed, when α-methylbenzyl alcohol was subjected to the same reaction conditions, styrene and polystyrene were obtained.

Fe^{3+}-SWy-1 calcined at 300°C was found to be inactive for the hydration of styrene perhaps because of the collapse of the interlayer structure of the catalyst since the basal spacing decreased from 14.3 to 9.7 Å (Table 1, entries 3 and 4). This result suggests that the access to the clay interior is a prerequisite for efficient catalysis. The pillared catalysts, air dried or calcined at 300°C (PIL.Fe^{3+}-SWy-1), were also inactive. Several other iron-exchanged clays were tested for the hydration of styrene. Among these, Fe^{3+}-SHCa-1, Fe^{3+}-STx-1 and Fe^{3+}-Thiomont [27] were inactive, while an air dried Nontronite, Fe^{3+}-NG-1, (Fe^{3+} content = 4.5 wt%, d_{100} = 12.9 Å) lead to the desired alcohol in 4% yield and 92% selectivity (Eq. (1)).

$$\text{(1)}$$

Yield = 4%, Selectivity = 92%, TON = 10
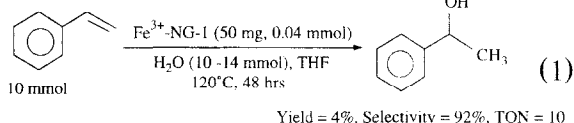
Various styrene derivatives were hydrated (Eq. (2)) and gave satisfactory results except 4-vinylanisole which leads to many unidentified products and 4-chlorostyrene which is unreactive (Table 4).
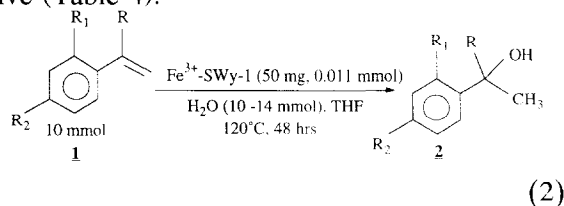
$$\text{(2)}$$

Fig. 2. Hydration of styrene with water (10 to 14 mmol) catalyzed by Fe^{3+}-SWy-1 (50 mg, 0.011 mmol) in THF at 120°C for 48 h.

Table 4
Hydration of various styrene derivatives using Fe^{3+}-SWy-1

Entry	1, R =, R_1 =, R_2 =	Yield (%)	Selectivity (%)	TON
1	R = CH_3, R_1 = H, R_2 = H	5	92	47
2 [a]	R = H, R_1 = H, R_2 = CH_3O	0	—	0
3	R = H, R_1 = H, R_2 = Cl	0	—	0
4	R = H, R_1 = H, R_2 = CH_3	6	86	56
5	R = H, R_1 = CH_3, R_2 = H	6	89	56
6	R = H, R_1 = CH_3, R_2 = CH_3	6	77	56

[a] The reaction gave more than 10 unidentified products.

3.2.1. Conclusions

Fe^{3+}-SWy-1 is an useful catalyst for the hydration of styrene derivatives. The hydration process is sensitive to the reaction conditions, with good efficiency attained using THF as the solvent, at 120°C using an approximately 900/1 ratio of substrate to catalyst. The highest turnover for the hydration of styrene was 65.

Acknowledgements

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