Vapor phase Beckmann rearrangement of cyclohexanone oxime over a novel tantalum pillared-ilerite

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The vapor phase Beckmann rearrangement of cyclohexanone oxime has been studied using a novel tantalum pillared-ilerite as catalyst: the cyclohexanone oxime conversion rate reaches 97.1% and the selectivity for ε-caprolactam is up to 89.1% at 350 °C.

Sulfuric acid as a catalyst plays an essential role in the industrial mass production of ε-caprolactam, a raw material for nylon-6. However, it poses significant environmental and operational problems such as generating undesirable salt and causing equipment corrosion. To overcome these problems, a number of heterogeneous catalysts for the vapor phase Beckmann rearrangement of cyclohexanone oxime have been proposed. Among typical heterogeneous catalysts for this reaction include solid acid catalysts such as boric acid, silica–alumina, zeolites like Y, ZSM-5, TS-1, B-ZSM-5 and tantalum oxide on silica.[1–4] Highly siliceous ZSM-5 and ZSM-5 modified with boron showed high activity and selectivity in the Beckmann rearrangement reaction.[5] However, the catalysts gradually deactivated with time. Solid acid catalysts of high activity with long catalytic lifetime are still under investigation.

Various types of hydroxy groups in amorphous silica or zeolites have been investigated as catalytically active sites for the Beckmann rearrangement reaction. A majority of researchers found that neutral or weakly acidic hydroxy groups present on the external surface of zeolites are effective for the Beckmann rearrangement reaction, whereas Brönsted acid sites of zeolites accelerate the formation of by-products.[6,7] This is suggestive that an efficient solid acid catalyst for the rearrangement reaction can be obtained if the catalyst is designed to include not only a controlled acidity but also a sufficient number of hydroxy groups.

In our study, an efficient solid acid catalyst for the vapor phase Beckmann rearrangement reaction is designed using layered silicates. A small amount of metal was intercalated between the silicate layers by the usual pillaring process to generate moderate acidity as a mixed oxide and to increase the thermal stability of the layered silicate for use in catalysis. Layered silicates, such as kanemite ($NaHSi_2O_5 \cdot 3H_2O$), magadiite ($Na_2Si_{14}O_{29} \cdot 11H_2O$), kenyaite ($K_2Si_{20}O_4 \cdot 11H_2O$), makatite ($Na_2Si_4O_9 \cdot 5H_2O$) and ilerite ($Na_2Si_8O_{17} \cdot xH_2O$) are composed of tetrahedral silicate sheets only and the each silicate sheet is terminated by hydroxy groups.[8] Layered silicates, therefore, possess abundant hydroxy groups oriented in a crystallographically regular manner, and have a great potential to act as new catalysts for the vapor phase Beckmann rearrangement reaction.

Here, the synthesis, characterization and catalytic application to the Beckmann rearrangement reaction of layered silicate catalysts pillared with tantalum oxide is presented.

Na-ilerite ($Na_2Si_8O_{17} \cdot xH_2O$) was synthesized hydrothermally at 100 °C for two weeks from a suspension of Ludox-HS 40 and NaOH solution with a molar ratio of $SiO_2 : NaOH : H_2O = 1 : 0.5 : 7$.[9] H-ilerite was prepared by acid titration of Na-ilerite. A suspension of Na-ilerite in water was titrated with 0.1 M HCl to a final pH of 2.0 and allowed to stand with stirring for an additional 24 h. The H-ilerite was recovered by filtering off, washing, and was dried at 40 °C. The sodium content of the sample was 0.11 wt% as determined by atomic absorption spectroscopy. Octylamine intercalation was performed to increase the interlayer spacing of ilerite by allowing H-ilerite to react with an excess of octylamine at room temperature.

The pillar precusor for tantalum oxide pillaring was prepared by the hydrolysis of tantalum pentaethoxide.[10] A small amount of octylamine was added to the solution to increase the degree of hydrolysis of tantalum pentaethoxide. The molar ratio of $Ta(OC_2H_5)_5 : H_2O :$ octylamine was adjusted to $1 : 12 : 0.3$. The pillar precusor can be represented as $Ta_xO_y(OR)_z$. For comparison, silicon pillared-ilerite was prepared according to the procedure in the literature.[9] The pillar precusor for silicon oxide pillaring was prepared by mixing octylamine and TEOS in the molar ratio of 2 : 5. The pillar precusor solution was added dropwise to the octylamine-ilerite gel with continuous stirring. The final suspension was allowed to stand for three days with stirring at room temperature. The resultant product was washed with ethanol, filtered off and dried at 100 °C. Samples were calcined at 700 °C for 1 h to eliminate residual organic molecules. The tantalum content of tantalum pillared-ilerite samples, as determined by inductively coupled plasma (ICP) spectroscopy, ranged from 3.8 to 5 wt%.

The as-synthesized metal pillared-ilerites have basal spacings of 27.2 Å (Ta) and 29.4 Å (Si) much larger than those of Na- and H-ilerites, (11.1 and 7.4 Å, respectively).[9] Although the basal spacings gradually decreased with increase in calcination temperature, the structures of the metal pillared-ilerites were preserved even after calcination at 700 °C (Fig. 1). Broad peaks in the XRD powder diffraction patterns indicate that poorly ordered structures are formed in metal pillared-ilerites. The N_2 adsorption–desorption isotherm of tantalum pillared-ilerite after complete elimination of organic molecules showed type IV behavior according to the BDDT classification. At high relative pressure ($P/P_o > 0.6$), hysteresis is observed owing to capillary condensation in mesopores, caused by pillaring of the layered silicates.

The BET surface areas of samples calcined at 700 °C are 395 $m^2\ g^{-1}$ for tantalum pillared-ilerite and 358 $m^2\ g^{-1}$ for silicon pillared-ilerite, much larger than those of the H- and Na-ilerites, (20 and 40 $m^2\ g^{-1}$, respectively).

The acidic properties of the tantalum pillared-ilerite was studied to identify the inherent acidity caused by incorporation of tantalum oxide between the layers of ilerite. In addition, the acidic properties of silicon pillared-ilerite was investigated to compare inherent acidities caused by incorporation of Ta or Si between the layers of ilerite. Acidities were determined by carrying out NH_3-TPD experiments. The TPD profile of the tantalum pillared-ilerite exhibits a broad desorption peak with a maximum at 220 °C. On the other hand, the silicon pillared-ilerite shows no desorption peak. This implies that tantalum pillared-ilerite contains a large number of acid sites of moderate acidity, whereas silicon pillared-ilerite shows no acidity.

The Beckmann rearrangement of cyclohexanone oxime was conducted using a continuous flow reactor under atmospheric

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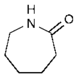
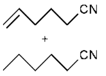
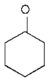
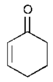
Table 1 Vapor phase Beckmann rearrangement of cyclohexanone oxime over various metal pillared-ilerites[a]

Catalyst	t/h	Conv. (%)	Selectivity (%)			
						
Ta-Ilerite	2	97.1	89.1	5.9	3.0	2.0
	8	96.9	85.7	9.3	3.1	1.8
Si-Ilerite	2	70.4	80.6	2.4	11.2	5.1
	8	30.5	54.2	7.8	26.3	11.7
Silicalite-1[b]	2	92.6	93.0	3.8	2.0	1.2
	8	89.1	89.8	5.1	3.7	1.4

[a] *Conditions*: T = 350 °C, P = 1 atm, WHSV = 0.5 h^{-1}, cyclohexanone oxime : EtOH : He = 1 : 9 : 10, Time on stream = 8 h. [b] Silicalite-1 was synthesized at 150 °C for 5 days using the mol ratio 0.1 TPABr : 0.2 NaOH : 1.0 SiO_2 : 35 H_2O.

pressure. Cyclohexanone oxime was dissolved in ethanol and injected with syringe pump at a WHSV of 0.5 h^{-1} under He flow with reaction carried out at 350 °C. The product was analyzed by GC using an SE-54 column.

The results of the rearrangement reaction over tantalum pillared-ilerite are shown in Table 1. The catalytic activity of tantalum pillared-ilerite was compared to Silicalite-1 (pure silica ZSM-5), which is known as the most selective catalyst for the vapor phase Beckmann rearrangement of oxime to lactam (Table 1). The tantalum pillared-ilerite showed a higher conversion of oxime than silicalite-1 while the selectivity for lactam over tantalum pillared-ilerite was slightly lower than that over silicalite-1. Also, the data was compared with that of silicon pillared-ilerite to investigate the effect of the metal as a pillar. For the tantalum pillared-ilerite catalyst, the cyclohexanone oxime conversion rate reaches 97.1% and the selectivity for ε-caprolactam is 89.1% at 350 °C. Tantalum pillared-ilerite catalyst is superior to the silicon pillared-ilerite in terms of both conversion and selectivity. Silicon pillared-ilerite shows quite high conversion and selectivity initially owing to inherent hydroxy groups from its layered features. However, it is rapidly deactivated within 8 h, which may be explained by the fact that it does not possess the moderate acidity required to catalyze the rearrangement reaction (ammonia TPD).

Although the exact role of the metal is not yet fully understood, it can be speculated that acidity of hydroxy groups in the metal pillared-ilerite is controlled by the metal used as pillar. The acid strength of the assumed species –Ta–O–Si–OH generated by the pillaring process is adequate enough to catalyze the rearrangement reaction.

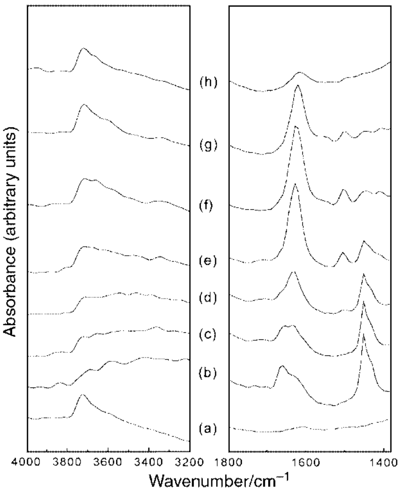


Fig. 1 FTIR spectra of tantalum pillared-ilerite measured at different temperatures (a) before and (b–h) after adsorption of cyclohexanone oxime [(a) 25, (b) 70, (c) 100, (d) 140, (e) 200, (f) 300, (g) 400 and (h) 550 °C]. These data were recorded on FTS-175 BIO-RAD FT-IR spectrometer.

FTIR spectra were measured for metal pillared-ilerite samples to elucidate the reaction pathway in detail. FTIR experiments were conducted using an *in situ* IR cell (Graseby, specac). Metal pillared-ilerite pellets were preheated at 550 °C under vacuum for 1 h. After the samples were cooled to room temperature, FTIR spectra were recorded [Fig. 1(a)]. One drop of a 1% ethanol solution of cyclohexanone oxime was added to the pellet held in the *in situ* cell under He gas flow. After the evacuation of physically adsorbed oxime at room temperature for 1 h, FTIR spectra were recorded at increments of 20 °C min^{-1} [(Fig. 1(b)–(h)].

The IR spectrum of tantalum pillared-ilerite [Fig. 1(a)] shows absorption bands of hydroxy groups[11] at *ca.* 3700 cm^{-1}. However, these bands disappeared upon adsorption of cyclohexanone oxime and new bands appeared at 1450 and 1663 cm^{-1} due to characteristic vibrations[12] of CH_2 and C=N groups of cyclohexanone oxime, respectively. This indicates strong interaction between the hydroxy groups of the catalyst and the reactant. For the temperatures above 100 °C, the characteristic vibration modes[12] of C=O and N–H of ε-caprolactam at 1635 and 1505 cm^{-1} were detected. However, with a stepwise rise of evacuation temperature, the C=O and N–H absorptions of ε-caprolactam were weakened around 400 °C and completely disappeared at 500 °C. The desorption temperature of the produced ε-caprolactam is shifted to a higher value than that observed in the catalytic reaction and might be due to the fast temperature increase rate in the FTIR experiment. IR spectra of silicon pillared-ilerite taken at different temperatures were similar to those of tantalum pillared-ilerite. However, the intensities of bands at 1635 and 1505 cm^{-1} due to the characteristic vibrations of C=O and N–H groups of ε-caprolactam were lower than those on tantalum pillared-ilerite, which implies that silicon pillared-ilerite has a low catalytic activity.

From the FTIR data, it is seen that the rearrangement to ε-caprolactam from cyclohexanone oxime over the tantalum pillared-ilerite takes place around 100 °C, while the desorption of the produced ε-caprolactam occurs at a higher temperature ($>$350 °C). Also this data strongly suggests that the hydroxy groups are active sites as reported for other zeolite catalysts.[6,7]

In conclusion, we report the synthesis and characterization of a novel tantalum pillared-ilerite that is shown to be a new advantageous catalyst for the vapor phase Beckmann rearrangement of cyclohexanone oxime. The excellent catalytic performance of tantalum pillared-ilerite for the Beckmann rearrangement reaction is ascribed to a large number of well dispersed hydroxy groups over the interlayer surface of tantalum pillared-ilerite and their relatively weak acidity.

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