

EFFECT OF LOADED ALKALI METALS ON THE STRUCTURAL, BASICITY AND CATALYTIC ACTIVITY OF ZEOLITE BETA

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Abstract: Zeolite Beta was modified by incorporation of an alkali metal (Na, K, Cs) through wet impregnation method. The incorporation of the base guests has reduced the crystallinity and BET surface area of zeolite Beta, as evidence by XRD, IR and nitrogen adsorption characterizations. The framework structure was totally collapsed at $\geq 8\%$ w/w loading of Na and K. Nevertheless, the concentration of base sites (basicity) was enhanced as evidence by the increase in the amount of desorbed CO_2 in TPD- CO_2 as the amount of metal loading increases. The catalytic activity of the modified samples was tested in dehydration-dehydrogenation of cyclohexanol. Selectivity of cyclohexanone that is produced on base sites of zeolite Beta increased with the increase in the basicity, consequently suppressed the selectivity of cyclohexene produced at acidic sites. Cyclohexene was obtained as the dominant product due to the dominant acidic properties of zeolite Beta. The ratio of cyclohexene to cyclohexanone varies with the increase in the metal loading.

Keywords: Base zeolite Beta, alkali metal, basicity, dehydration-dehydrogenation of cyclohexanol

Abstrak: Zeolit beta diubahsuai dengan memasukkan logam alkali (Na,K,Cs) kepada zeolit melalui kaedah pengisitepuan basah. Kehadiran logam alkali ini telah menurunkan kehabluran dan luas permukaan BET zeolit beta menurut keputusan pencirian sampel melalui XRD, IR dan penyerapan nitrogen. Bingkai zeolit musnah pada muatan Na dan K, $\geq 8\%$ w/w. Sebaliknya kepekatan tapak bes meningkat seperti yang dibuktikan daripada peningkatan penyerapan CO_2 dengan kaedah TPD- CO_2 dengan peningkatan amaun muatan logam. Aktiviti mangkin sampel yang diubahsuai diuji dalam tindak balas nyahhidratan-nyahhidrogenan sikloheksanol. Kepilihan sikloheksanon yang terhasil pada tapak bes zeolit beta meningkat dengan peningkatan kebesan, yang seterusnya menahan kepilihan terhadap sikloheksena terhasil di tapak asid zeolit. Namun, sikloheksena masih lagi merupakan hasil utama disebabkan sifat asid zeolit beta yang lebih dominan. Nisbah sikloheksena kepada sikloheksanon berubah-ubah dengan peningkatan muatan logam alkali.

Kata kunci: zeolit Beta berbes, logam alkali, kebesan, nyahhidratan-nyahhidrogenan sikloheksanol

1.0 INTRODUCTION

The knowledge of basicity enhancement in zeolite by cation exchange and incorporation of new species, such as hydroxides, oxides, and alkaline metal clusters, has been used for many years [1]. At the beginning of the 1990s, zeolites were used as base

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catalysts in their ion exchange and impregnate forms. Ion exchanged zeolites possess only low strength of base sites. In order to create stronger base sites in the cavities of zeolites, impregnation with various alkali salts was carried out. The base sites of the guest oxides were shown to be stronger than those of the zeolitic framework [2].

The main obstacle in preparing base zeolite is the low resistance of the framework structure towards basicity, wherein the structure will collapse due to the hydrolysis of Si-O-Al bond in the zeolite framework. In this work, zeolite Beta was chosen to be modified into base catalysts due to its large pore structure which is desirable for catalysts modification and catalytic activity by larger organic molecules. It also has the potential in exhibiting base property that is greater than expected from its chemical composition alone [1].

In this study, zeolite Beta with base property was prepared by introducing an alkali metal (Na, K and Cs) through wet impregnation method. The structural and basicity properties of the samples were characterized by XRD, FTIR, nitrogen adsorption and TPD-CO₂ in order to correlate their catalytic activity in the dehydration-dehydrogenation of cyclohexanol as model reaction.

2.0 EXPERIMENTAL

2.1 Preparation of the Catalysts

Zeolite Beta in hydrogen form (HBeta) with SiO₂/Al₂O₃ = 25 supplied by Zeolyst was used as the starting material. Catalysts were prepared by wet impregnation using the alkali metal acetate (Na, K and Cs) with various percentages [3]. Alkali metal acetate was dissolved in distilled water and then added to zeolite HBeta. The mixture was mixed homogeneously using a magnetic stirrer. The ratio of the weight of zeolite to the volume of distilled water used to dissolve the metal salt was 1:3. The mixture was left to dry slowly in a desiccator containing silica gel, by stirring overnight, followed by oven drying at 100°C overnight. The dried samples were calcined at 500°C for 6 hrs in air with a heating rate of 1°C/min where the metal salt decomposed into its oxide form. Samples were labeled as stated in Table 1.

2.2 Characterizations

The prepared samples were characterized by XRD, IR and nitrogen adsorption. The XRD diffractogram was recorded on D500 Siemens Kristalloflex X-ray diffractometer with CuK_α as the radiation source with $\lambda = 1.5418 \text{ \AA}$ at 40 kV and 30 mA. Diffractions were measured in the range of 2θ of 2° to 60° at room temperature with step time of 0.02°/s. The infrared spectra was recorded at room temperature with 4 cm⁻¹ resolutions between 4000-400 cm⁻¹ by using FTIR Perkin Elmer 1600 series. The BET surface area of the modified catalysts were determined by nitrogen adsorption using automated adsorption instrument Micromeritics ASAP 2010 model as well as ThermoFinnigan Qsurf Surface Area Analyzer M1-M3.

The basicity of the prepared base zeolite Beta was measured by TPD-CO₂, acquired by using TPD/R/O 1100 ThermoFinnigan. Sample (0.15-0.25 g) was pretreated in a flow of nitrogen at 400°C for 2 hrs. The sample was then exposed to CO₂ at a rate of 20 mL/min for 30 min at 40°C. The temperature was then raised gradually from 40-600°C. The desorbed gases were analyzed by Thermal Conductance Detector (TCD). The TPD-ammonia was also carried out using the same conditions as the TPD-CO₂. The samples were pretreated at 450°C and the NH₃ was adsorbed at 80°C.

2.3 Catalytic Reaction

Dehydration-dehydrogenation of cyclohexanol was carried out using a down-flow, fixed bed reactor of 8 mm internal diameter at atmospheric pressure [4]. The catalyst (0.1 g) was pretreated in the reactor at 300°C for 2 hrs. Oxygen was then passed through the catalytic bed and followed by feeding of the reactant at the flow rate of 6 mL hr⁻¹. The reaction was carried out at 300°C for 1 hr. The product in liquid form was collected at the bottom of the reactor and analyzed by a Hewlett Packard Model 5880A gas chromatography with Flame Ionization Detector (FID). Analysis was carried out from 40-200°C at the heating rate of 10°/min by using Phase AT-WAX capillary column (diameter 0.25 mm, film thickness 0.2 μm, length 30 m).

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties

The XRD diffractograms for samples of Na- and K-impregnated HBeta after calcination are shown in Figures 1 and 2. The samples are noted as Na-X or K-X where X denotes the percentage of metal loading. The diffraction pattern for samples with 1 - 4%w/w of metal loadings (Na-1, Na-2 Na-4, K-1, K-2, K-4) shows similar pattern to that of the parent HBeta as indicated by the diffraction peaks at $2\theta = 7.8^\circ, 16.5^\circ, 2.15^\circ, 22.5^\circ, 25.3^\circ, 26.9^\circ, 29.5^\circ$ and 43.5° . The presence of all the typical XRD peaks for zeolite Beta [5], indicates the framework structure has been retained after loaded with these percentages of sodium and potassium. However, diffractograms for samples Na-6 and K-6 show partial amorphous phase suggesting that the framework of zeolite Beta have partially collapsed. Meanwhile, samples Na-8 and K-8 have turned into completely amorphous, indicating a total collapse of the zeolite framework.

On the other hand, framework structures of Cs-impregnated HBeta samples were retained even at 8%w/w of cesium loading (Figure 3). Since cesium has far higher atomic weight compared to sodium and potassium, in a same %w/w of alkali metal in zeolite Beta, cesium has the lowest number of mole. Consequently, the framework was not affected by the presence of cesium with the small amount of cesium loading.

There is no indication of the presence of any crystalline phase such as alkali metal (Na, K, Cs) acetate or new alkali metal phase, other than the Beta phase. It shows that

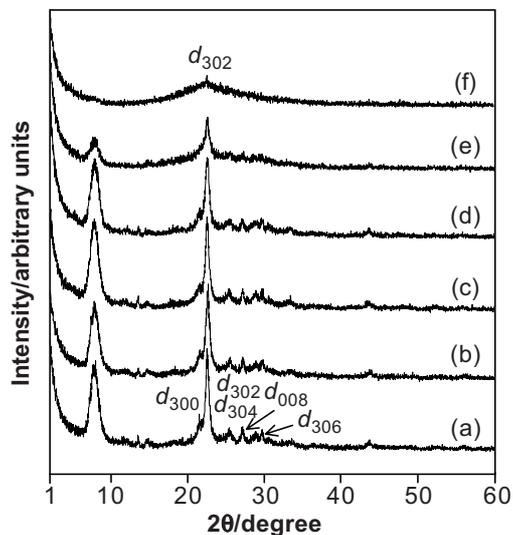


Figure 1 X-ray diffraction patterns of the sodium impregnated HBeta after calcination: (a) HBeta, (b) Na-1, (c) Na-2, (d) Na-4, (e) Na-6, (f) Na-8. The number denotes % of metal loading

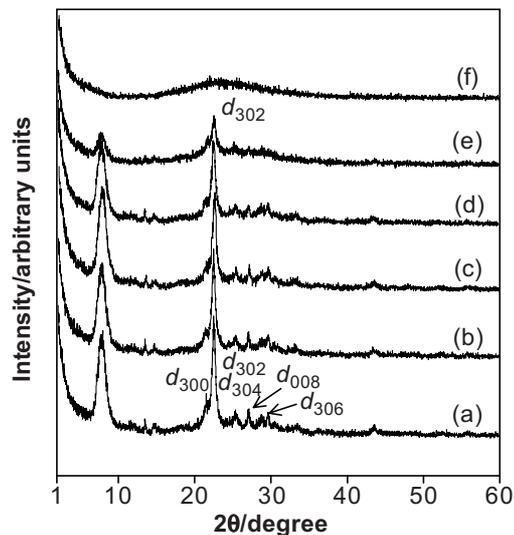


Figure 2 X-ray diffraction patterns of the potassium impregnated HBeta after calcination: (a) HBeta, (b) K-1, (c) K-2, (d) K-4, (e) K-6, (f) K-8. The number denotes % of metal loading

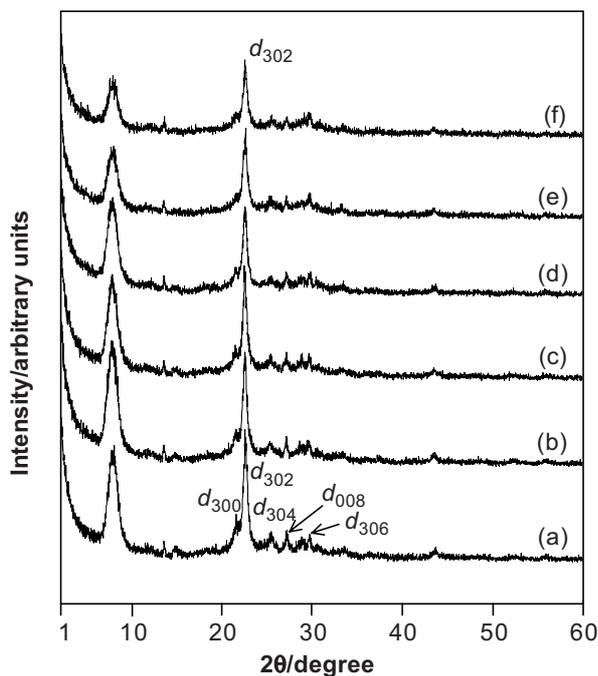


Figure 3 X-ray diffraction patterns of the cesium impregnated HBeta after calcination: (a) HBeta, (b) Cs-1, (c) Cs-2, (d) Cs-4, (e) Cs-6, (f) Cs-8. The number denotes % of metal loading

the alkali metal salt or oxides are well dispersed on the surface of zeolite Beta crystal [6]. However, the intensity of XRD peak at $2\theta = 22^\circ$ decreases with the increase in metal loading, indicating the decrease in the crystallinity of zeolite Beta framework structure (Table 1). The relative crystallinity of both sodium and potassium impregnated zeolite Beta decreased successively with an increase of the metal loading. The degree of crystallinity of potassium impregnated HBeta sample was found to be lower compared with the sample of sodium impregnated HBeta. This might be due to the higher alkalinity of potassium, as the potassium is more electropositive than sodium. Thus, it is expected that the hydrolysis of Si-O-Al will be greater in potassium-impregnated samples. Conversely, the crystallinity of cesium impregnated samples decreased monotonously due to the lesser number of mole Cs loading.

The results revealed that the presence of alkali metal oxides affected the thermal stability of zeolite Beta, leading to the deterioration and collapsed of the framework structure when calcined at elevated temperature. This may be due to the hydrolysis of Si-O-Al bond by alkali during calcination. Apart from that, the formation of alkali metal-aluminosilicate due to the strongly base condition during the impregnation procedure may also lead to partial damage of zeolite framework [7].

Table 1 Properties of alkali metal impregnated zeolite Beta

Sample	Metal loading (%w/w)	Relative crystallinity (%) ^a	BET surface area (m ² /g) ^b	Amount of desorbed CO ₂ ^c	
				(μ mole/g)	(moleCO ₂ /mole metal)
HBeta	0	100.00	558.63	6.27	–
Na-1	1	96.86	550.69 ^d	10.02	23.02
Na-2	2	91.31	546.17 ^d	14.61	16.79
Na-4	4	75.58	448.14	28.03	16.11
Na-6	6	43.05	295.20 ^d	40.63	15.57
Na-8	8	0.00	70.95	43.36	12.46
K-1	1	81.37	556.29 ^d	6.74	26.33
K-2	2	79.29	522.83 ^d	7.34	14.35
K-4	4	65.67	441.90	15.81	15.45
K-6	6	35.34	289.05 ^d	38.29	24.95
K-8	8	0.00	77.81	46.87	22.91
Cs-1	1	85.82	521.63 ^d	9.96	132.76
Cs-2	2	84.01	528.24 ^d	7.37	48.91
Cs-4	4	65.17	490.37	9.84	32.70
Cs-6	6	67.45	477.51 ^d	8.40	18.59
Cs-8	8	55.94	492.14	7.69	12.78

^a Intensity of the peak at $2\theta 22^\circ$ in comparison with the parent HBeta (%)

^b Determined by nitrogen adsorption using BET technique (Micromeritics ASAP)

^c Amount of desorbed CO₂ determined by TPD-CO₂

^d ThermoFinnigan Qsurf Surface Area Analyzer

The BET surface area of zeolite Beta was found to decrease as the metal loading increased (Table 1). This could be attributed to the dissolution of part of the framework during impregnation and pore filling by the alkali oxides [8]. This is supported by the fact that the BET surface area decreases linearly as a result of the decrease in the crystallinity of zeolite Beta framework with the value of calibration curve R^2 of 0.9319. The drastic decreased of about 87 and 86% in the BET surface area of samples Na-8 and K-8, respectively in comparison to HBeta, indicated the collapse of the framework structure. On the other hand, the BET surface area of Cs-8 sample still remained more or less similar to that of the HBeta. This findings support the results obtained from XRD and IR analyses indicating that the framework structure of Cs-8 was still retained even at 8%w/w Cs loading.

3.2 Basicity Study

The TPD- CO_2 thermograms of sodium impregnated zeolite Beta samples are as shown in Figure 4, while the data of TPD of desorbed CO_2 are presented in Table 1. It was observed that most of the CO_2 was desorbed from the catalyst at temperature below 200°C with the maximum desorption peak at around 100°C . This indicates the presence of weak base sites in zeolite Beta where at this temperature range, the CO_2 is physically attached to the surface of the zeolite Beta samples. Both potassium (Figure 5) and cesium (Figure 6) impregnated zeolite Beta showed similar results as the sodium impregnated samples.

The shift of the desorption peak to a slightly higher temperature in samples Na-6, Na-8, K-6 and K-8 implies a slight increase in basicity of these samples. It suggests that the bulkier loading of sodium may have forced the occupancy of the sodium oxides into the small cages of the zeolites (i.e. double six or four rings cages) rather than in the channel systems. A slightly higher energy is needed to desorb the CO_2 attached like this fashion (in the small cages) and thus resulting in higher temperature for desorption for these samples. However, the strength of the basicity of sample Na-8 and K-8 is slightly lower in which the maximum desorption temperature occur at slightly lower temperature than samples Na-6 and K-6. This may be due to the fact that the framework structure of zeolite Beta at 8%w/w of sodium and potassium loading may have collapsed causing the sodium oxides dislocated on to the amorphous surface of SiO_2 and Al_2O_3 .

Even though CO_2 adsorbed weakly on the catalysts, the obtained TPD data do reveal some correlation in the basicity of the catalysts. The basicity of parent HBeta increased to about 60% or more than 2-fold, respectively with the 1% and 2% w/w loading of sodium (Table 1). The basicity was found to increase with an increase of the percentage of sodium loading, in which it achieved 7-fold increment in 8%w/w of sodium loading. The base guest, i.e. sodium oxide was found to contribute to the basicity that was created after calcinations at high temperature. However, an additional desorption peak was observed in sample Na-6 which might be contributed by the

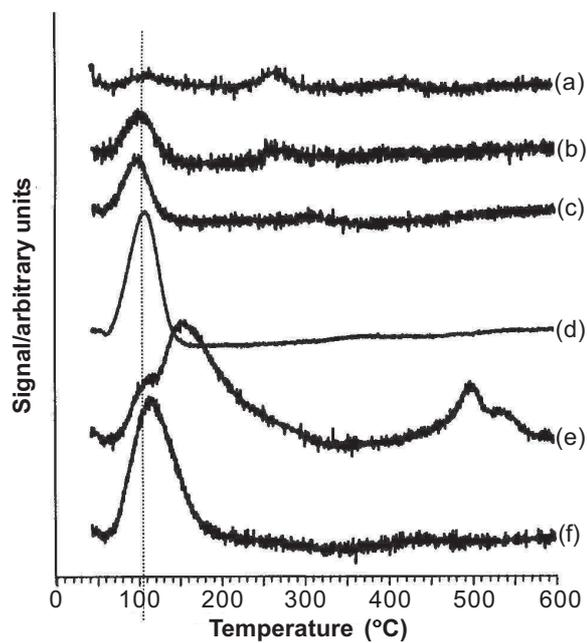


Figure 4 TPD-CO₂ thermograms of the sodium impregnated HBeta: (a) HBeta, (b) Na-1, (c) Na-2, (d) Na-4, (e) Na-6, (f) Na-8. (The number denotes % of metal loading)

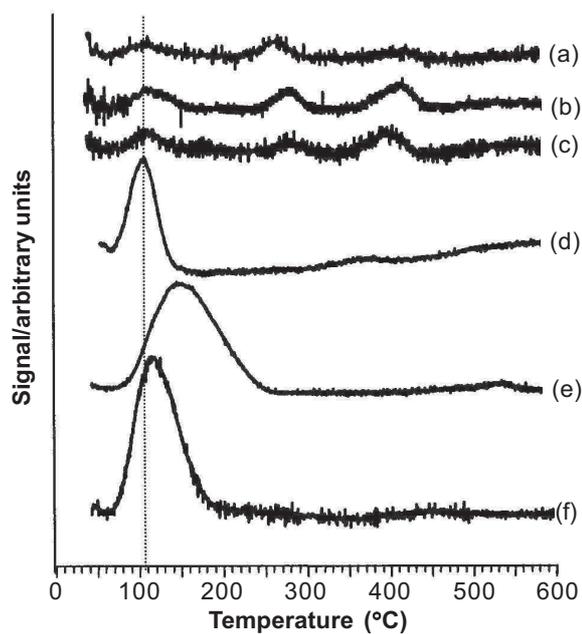


Figure 5 TPD-CO₂ thermograms of the potassium impregnated HBeta: (a) HBeta, (b) K-1, (c) K-2, (d) K-4, (e) K-6, (f) K-8. (The number denotes % of metal loading)

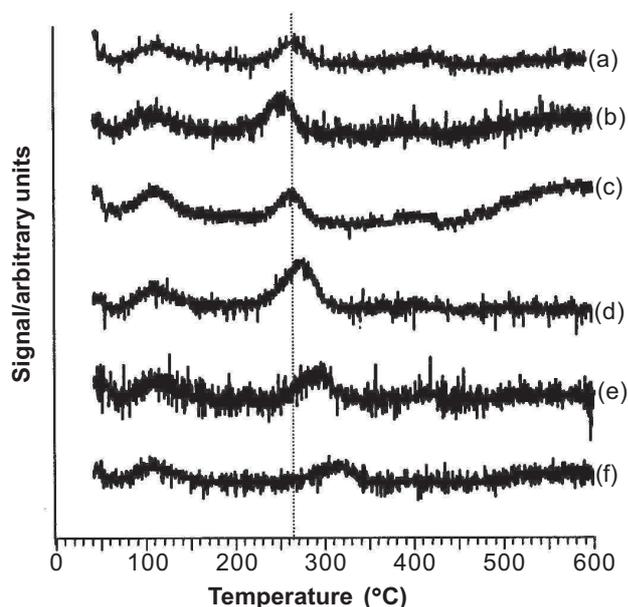


Figure 6 TPD- CO_2 thermograms of the cesium impregnated HBeta: (a) HBeta, (b) Cs-1, (c) Cs-2, (d) Cs-4, (e) Cs-6, (f) Cs-8. (The number denotes % of metal loading)

decomposition of acetate residue, such as acetate, in the sample. Meanwhile, the basicity remained the same when 1%w/w and 2%w/w of potassium were loaded into zeolite Beta samples (Table 1). However, the basicity increased more than 2-fold when 4%w/w of potassium was loaded. The basicity increased exponentially when 6%w/w and 8%w/w of potassium were impregnated, reaching $\sim 35 \mu\text{mole/g}$ and $\sim 45 \mu\text{mole/g}$, respectively.

Cesium oxide is known as a strong base. Thus, a higher basicity is expected when cesium oxide was introduced into zeolite Beta. However, the results showed no significant increment in the basicity. This may be due to the small amount of the number of mole cesium used to impregnate the zeolites (even at 8% loading.). Nonetheless, the base strength was enhanced slightly by the small amount of cesium introduced into HBeta. This could be seen as a slight shift of desorption peak at $\sim 260^\circ$ towards higher temperature as the cesium loading is increased, as shown in Figure 6.

In general, the number of basic sites created by the introduction of sodium into zeolite Beta framework is higher than potassium and cesium (Table 1), except for 8%w/w loading, which is slightly lower than sample K-8. Potassium is found to have a higher contribution to basicity strength in comparison to sodium, where it needs about 2-fold more amount of number of mole sodium in comparison to potassium in order to achieve the basicity ($> 40 \mu\text{mole/g}$) as contributed by potassium. The number of moles of CO_2 desorbed per mole of alkali metal was found to decrease as %w/w of the

metal loading increased. This may be due to the lower dispersion of metal oxides and the tendency to form metal oxides cluster in samples containing higher amounts of metal oxides [8]. The role of cesium as a highly alkali metal precursor was insignificant in this study, due to its small amount of mole cesium loading compared to that of the sodium and potassium impregnated zeolite Beta.

3.3 Catalytic Activity

The dehydration-dehydrogenation of cyclohexanol was used as the model reaction to test the catalytic activity of the alkali metal impregnated zeolite Beta. Results from the catalytic testing are summarized in Table 2.

By using alkali metal impregnated zeolite Beta as catalyst, the selectivity of cyclohexanone was found to increase as the amount of sodium and potassium loading increased, especially at a 6-8%w/w of metal loading with basicity higher than 30 $\mu\text{mole/g}$ (Figure 7). The significant increase in the selectivity of cyclohexanone from 4%w/w to 6%w/w loading is due to the slightly stronger basicity besides its higher amount of basicity alone. Meanwhile, the selectivity of cyclohexanone slightly dropped at 8%w/w loading of sodium and potassium due to the collapse of zeolite Beta framework, where the base strength is slightly lowered. The fact that the slightly weaker basicity, due to the collapsed zeolite Beta framework, causing the slight decrease in selectivity of cyclohexanone suggests that the framework of zeolite Beta does have an influence in catalyzing this reaction.

Table 2 Catalytic activity of alkali metals loaded zeolite Beta catalysts on the hydration-hydrogenation of cyclohexanol

Sample	Conversion (%)	Selectivity (%)		Cyclohexene / cyclohexanone
		Cyclohexene	Cyclohexanone	
HBeta	65.07	80.74	1.27	63.57
Na-1	97.27	95.45	1.46	65.38
Na-2	84.92	91.78	2.07	44.34
Na-4	38.56	51.93	3.93	13.21
Na-6	10.10	19.89	16.84	1.18
Na-8	13.56	20.02	10.38	1.93
K-1	90.72	91.41	1.29	70.87
K-2	92.50	98.51	1.16	84.92
K-4	77.82	95.79	1.52	63.02
K-6	17.91	10.27	8.56	1.20
K-8	16.39	0.00	5.76	0.00
Cs-1	78.80	93.66	1.53	61.22
Cs-2	98.50	97.85	1.47	66.56
Cs-4	89.41	97.56	1.59	61.36
Cs-6	89.62	93.34	1.58	59.08
Cs-8	75.08	97.46	1.69	57.67

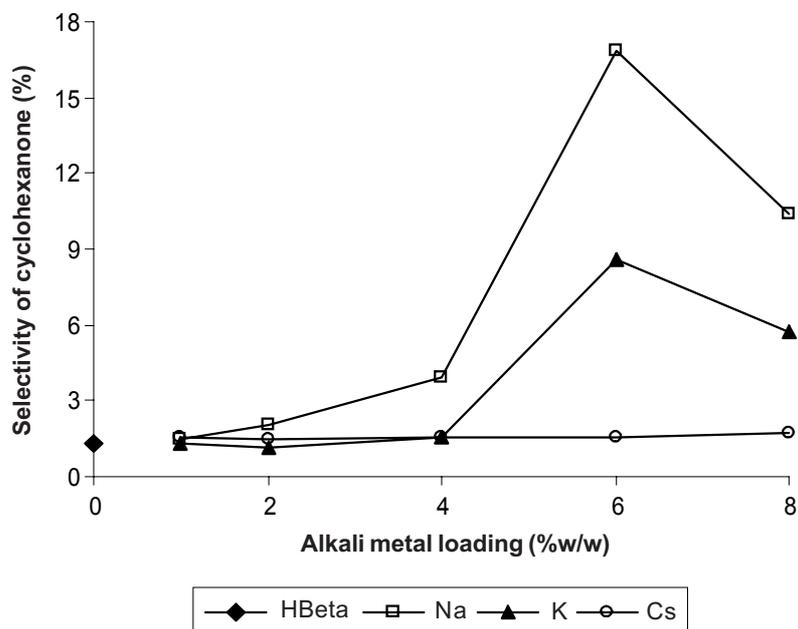


Figure 7 Influence of alkali metal loading (%w/w) on the selectivity of cyclohexanone

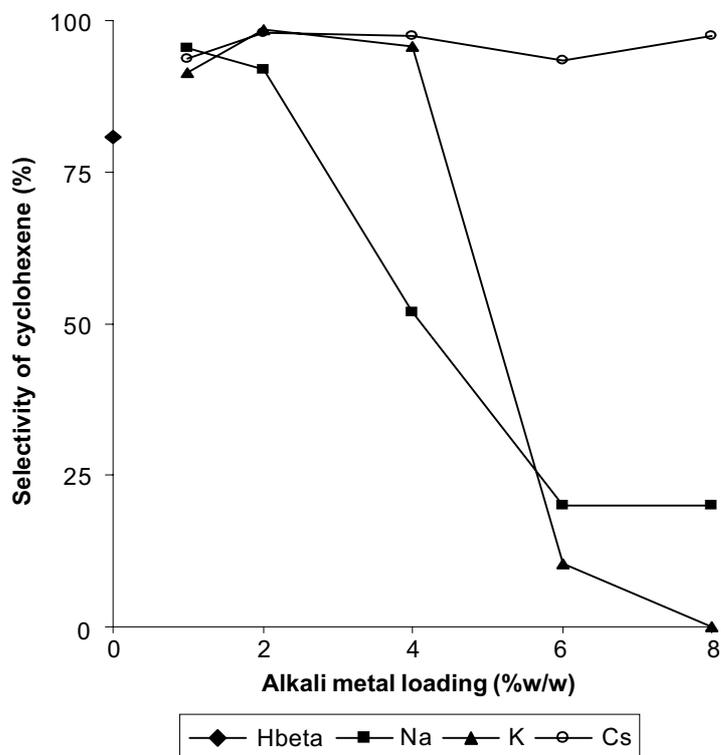


Figure 8 Influence of alkali metal loading (%w/w) on the selectivity of cyclohexene

The selectivity of cyclohexanone increased to about 7 and 5-fold for sample K-6 and K-8 compared to that of the parent HBeta (Table 2). The selectivity of cyclohexanone is even far more higher in sample Na-6 and Na-8 with 13 and 8-fold of increment respectively. The higher selectivity of cyclohexanone in sodium impregnated zeolite Beta than the potassium may be due to the larger amount of sodium that have been loaded, which is about 2-fold of milimole higher in comparison to potassium. There is no increment in the selectivity of cyclohexanone (Figure 7) when using the cesium impregnated zeolite Beta as catalyst (Cs-1 to Cs-8) due to the low basicity that has been created. Thus, cyclohexene which is produced at acid sites is largely obtained by using these catalysts with high selectivity, i.e. > 93%.

Cyclohexene is found to be the main product obtained in this reaction. This indicates that the basicity created by the introduction of an additional guest is incomparable to the inherently acidic properties in zeolite Beta. However, the higher percentage of alkali metal loading would suppress the selectivity of cyclohexene (Figure 8), except for cesium impregnated zeolite Beta. This shows some competition between acidic and basic properties in this reaction as the basicity increases (Table 2). The selectivity

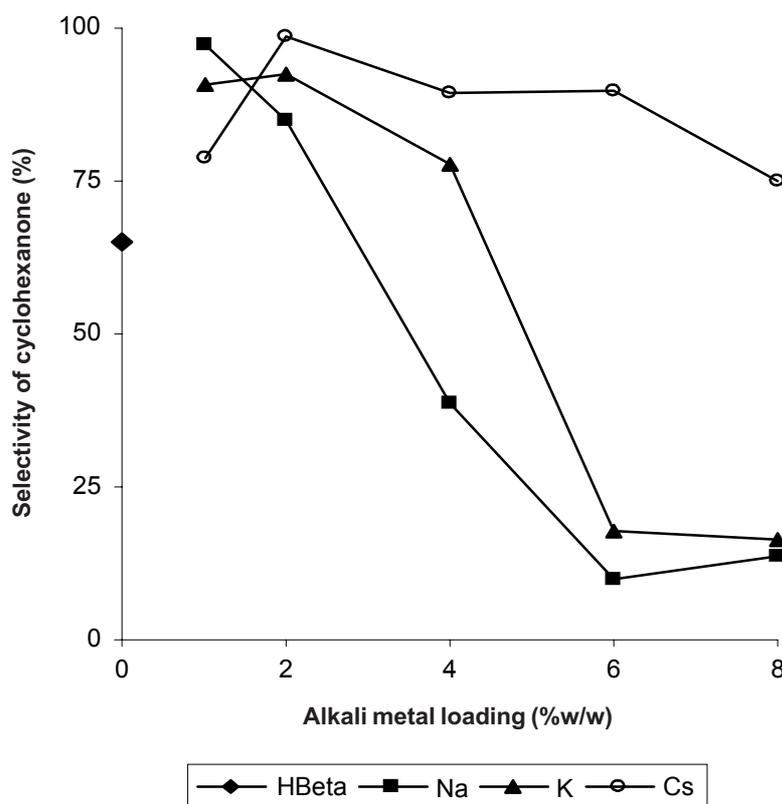


Figure 9 Influence of alkali metal loading (%w/w) on the conversion of cyclohexanol

of cyclohexene decreased significantly as 6-8%w/w of sodium and potassium was introduced into zeolite Beta. The ratio of selectivity of cyclohexene to cyclohexanone was found to decrease as the zeolite Beta loaded with alkali metals (Na and K). Thus, the increase in the basicity will suppress the acid sites in zeolite Beta causing the decrease in the selectivity of cyclohexene. The conversion of cyclohexanol (Figure 9) is also decreased in parallel with the decrease in selectivity of cyclohexanone and relative crystallinity.

4.0 CONCLUSIONS

The basicity of zeolite Beta was enhanced by the introduction of an additional alkali metal as a base guest. The basicity increased with the increase in the amount of metal loading but simultaneously decreased in both crystallinity and the surface area. At a higher amount of metal loading and elevated temperature, the stability of zeolite framework decreased due to the hydrolysis of Si-O-Al bond in the present of alkali metals. The selectivity of cyclohexanone increased with the increase of basicity. However, cyclohexene remains the main product in this reaction, indicating the basicity that has been created is still incomparable to the inherently acidic properties in zeolite Beta. The increased in basicity will inherently suppressed the acidic property in zeolite Beta, as evidence by the decrease in the ratio of cyclohexene to cyclohexanone. Samples of zeolite Beta loaded with 6%w/w Na and K respectively were found to be the best catalysts in this study, wherein the basicity was enhanced significantly without collapsing the framework structure of zeolite Beta besides increasing the selectivity of cyclohexanone.

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