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Article

NaOH modified WO_3/SiO_2 catalysts for propylene production from 2-butene and ethylene metathesis

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ABSTRACT

A WO_3/SiO_2 catalyst is used in industry to produce propylene from 2-butene and ethylene metathesis. Catalysts with various WO_3 loading (4% to 10%) were prepared by impregnation and tested for the metathesis of ethene and *trans*-2-butene. Ion exchange of NaOH onto the WO_3/SiO_2 catalyst was used to mitigate the acidity of the catalysts in a controlled way. At low WO_3 loading, the treatment with large amounts of NaOH resulted in a significant decrease in metathesis activity concomitant with significant W leaching and marked structural changes (XRD, Raman). At higher WO_3 loading (6% to 10%), the treatment with NaOH mainly resulted in a decrease in acidity. FT-IR experiments after adsorption of pyridine showed that the Lewis acidic sites were poisoned by sodium. Nevertheless, the metathesis activity remained constant after the NaOH treatment. This suggested that the remaining acidity on the catalyst was enough to ensure the efficient formation of the carbene active sites. Interestingly, Na poisoning resulted in some modification of the selectivity. The mitigation of acidity was shown to favor propene selectivity over the formation of isomerization products (*cis*-2-butene, 1-butene, etc.). Moreover, treatment with NaOH led to a shorter induction period and reduced coke formation on the WO_3/SiO_2 catalyst.

1. Introduction

Due to the rising demand for propylene in the petrochemical industry, the metathesis of 2-butene and ethylene is now used for on-purpose propylene production [1,2]. Several catalysts including supported MoO_3 [3,4], Re_2O_7 [5–7], and WO_3 [8–10] are known to catalyze the reaction. Industrially, the WO_3/SiO_2 system is the most common. The metathesis of light olefins has been developed since 1966 in a process known as the Phillips triolefin process, which was adapted as a licensed olefins conversion technology (OCT) by ABB Lummus Global, Houston (USA) for the production of propene [11]. Since then, many studies have been carried out to develop WO_3/SiO_2 catalysts with improved performance. The mechanism of the metathesis reaction of 2-butene and ethylene over the WO_3/SiO_2 catalyst involves the formation of W-carbene species on the WO_3 surface, followed by metathesis on these active sites to yield propylene [12]. Many factors affect catalytic activity including the method of catalyst preparation, reaction conditions, structure of the support, and nature of the surface tungsten

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species. Experimental studies have reported that tetrahedral tungsten oxide species are the active sites [11,13].

As compared to MoO_3- and Re_2O_7-based catalysts, supported tungsten oxide catalysts are active at higher reaction temperatures (300–500 °C) [1,14]. At these temperatures however, side reactions such as isomerization, oligomerization, and cracking of alkenes also occur, so the selectivity to primary metathesis products is usually decreased [2]. Huang et al. [15–17] found that Brönsted acidity promoted the formation of active metathesis sites. Andreini et al. [18] suggested that the formation of the initial metal carbene needed acidity on the catalyst. However, van Roosmalen and Mol [13] reported that isomerization occurs on the Brönsted acid sites of the WO_3/SiO_2 catalysts. This led to several recent studies that focused on poisoning the acid sites with small amounts of an alkali metal such as Na, K, Rb, and Cs [19,20]. Spamer et al. [20] found that branched metathesis products were decreased by the addition of small amounts of an alkali metal ion, that is, isomerization was reduced. However, excessive amounts of alkali led to a sharp decrease in the metathesis rate. Because the WO_3 catalyst is active at 300–500 °C, the formation of coke is expected to cause deactivation. Several studies looked at coke formation on the catalysts during olefin metathesis [21,22]. They showed that the mechanism of coke formation is promoted by acidity on the catalyst [21–24]. In this case also, alkaline doping can have a beneficial impact [22,25].

In the present study, we tested WO_3/SiO_2 catalysts that have different loading under conditions close to the industrial ones to evaluate the impact of Na poisoning. Infrared spectroscopy of pyridine adsorption was used to evaluate the impact of Brönsted and Lewis sites on metathesis activity. We discuss the effect of Na poisoning on the undesired side reactions, catalyst stability, and coke formation.

2. Experimental

2.1. Catalyst preparation

WO_3/SiO_2 catalysts with different tungsten loading were prepared by impregnation of silica gel (Davisil Grade 646, pore volume 1.15 cm^3/g, supplied by Aldrich) with an aqueous solution containing the desired amount of ammonium metatungstate hydrate (Aldrich, 99.9%). The impregnated sample was dried in ambient air for 2 h and subsequently in an oven at 110 °C for 24 h, following by calcination at 550 °C in air for 8 h. The catalysts were denoted as $x$$WO_3/SiO_2$, where x was the WO_3 weight loading (%) and referred to as pristine catalysts. Each calcined pristine catalysts (3.5 g) was ion exchanged with an aqueous NaOH solution (300 mL). The concentration of the solution was such that the number of NaOH molecules introduced in the ion exchange was equal to 0.5, 1.0, or 1.5 times the number of acid sites present on the catalyst (as determined by titration, vide infra). The suspension was stirred at room temperature for 2 h. After that, the solid was filtered off, and it was dried in an oven at 110 °C for 24 h followed by calcination. The sample obtained by this procedure was designated, e.g., as 4W+0.5NaOH, which denotes that 4%WO_3/SiO_2 was exchanged with a solution of NaOH, which could titrate half of the acid sites present on the catalyst. .

2.2. Characterization

The specific surface area, pore volume, and pore diameter of the catalysts were determined by N_2 adsorption on a Tristar (Micromeritics) instrument. Measurements were performed with nitrogen as the adsorbate at –196 °C after pretreatment of the sample at 200 °C under nitrogen flow for 12 h. The actual metal loading was determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 2100 DV instrument. Before the measurement, the sample was dissolved with hydrofluoric acid at 60 °C. X-ray diffraction (XRD) was performed to determine the bulk phase of the catalysts using a SIEMENS D 5000 instrument and Cu K_α radiation with a Ni filter in the 2θ range of 10° to 80° with a resolution of 0.04°. The crystallite size was calculated by Scherrer's equation.

Raman spectra of the samples were collected using a continuous wave YAG laser of Nd (810 nm) of 100 mW power with the sample at room temperature. A scanning range of 200 to 2000 cm^{-1} with a resolution of 16 cm^{-1} was used. The number of total acid sites was determined by a method involving an aqueous ion exchange of the catalyst H^+ ions with Na^+ ions, followed by the titration of the resulting solution [26]. Catalyst (0.2 g) was added to 10 mL of aqueous solution of NaCl (3.42 mol/L) under stirring. After 30 h of ion exchange at room temperature, the solid particle was filtered off, and the filtrate was titrated with aqueous NaOH solution (0.05 mol/L) to determine the number of exchangeable acid sites in μmol H^+/g-catalyst. Fourier transform infrared (FT-IR) spectroscopy of pyridine adsorption was used to characterize the Lewis and Brönsted acid sites. Each sample was pressed into a thin wafer (~30 mg). The wafer was outgassed at 300 °C for 2 h under vacuum and then cooled to room temperature, and the IR spectrum was recorded as the background spectrum. Subsequently, pyridine vapor was admitted into the sample chamber at 50 °C for 15 min. Next, pyridine was desorbed under vacuum for 0.5 h to remove physisorbed pyridine, and an IR spectrum was recorded. All IR spectra of the adsorbed species were obtained by subtracting the background spectrum. The coke content was determined by thermogravimetric analysis (TGA) using an SDQ T 600 equipment. The used catalysts were heated in a stream of 10%O_2-90%He at a 10 °C/min heating rate to 700 °C.

2.3. Catalytic testing

For activity testing, 3.0 g of catalyst was packed in the center of a stainless steel tubular reactor. The catalyst was pretreated at 550 °C under nitrogen flow for 1 h, and the reaction conditions were: temperature 400 °C, pressure 0.1 MPa, C_2H_4:*trans*-2-C_4H_8 molar ratio 2:1 (4% of C_2H_4 and 2% of *trans*-2-C_4H_8) balanced with N_2, and the total flow rate 90 cm^3/min. The composition of the product and feed streams were analyzed by a Shimadzu GC-2014 gas chromatograph equipped with an FID detector.

3. Results and discussion

3.1. Catalyst characterization

The total acidity of the pristine catalysts was determined by titration (Table 1). These values allowed us to perform the NaOH ion exchange in a controlled way by adding a specific amount of NaOH. The compositions of the pristine and modified catalysts were investigated by ICP-OES (Table 1). The WO_3 content was lower for the NaOH-treated catalysts, indicating that the treatment induced W leaching. However, the leaching effect was pronounced only for the catalyst with the lowest WO_3 loading (4%WO_3/SiO_2), for which a sharp decrease in WO_3 loading (by 75%) was observed after the ion exchange with the solution with the highest NaOH concentration. For all the other catalysts with higher tungsten loading, even with the treatment with the solution with the highest NaOH concentration, the amount of WO_3 leached was less than ~15%.

The textural structure of the catalysts was characterized by N_2 physisorption (Table 1). The specific surface area and pore volume decreased slightly with increasing tungsten loading while the average pore size remained unchanged. Thus the impregnation did not affect significantly the texture of the support, and it can be concluded that WO_3 was mainly deposited on the outer surface of the support (and not in the pores). The textural properties were not altered by the treatment with NaOH.

The XRD of the pristine catalysts showed that there was only partial dispersion of tungsten oxide because the characteristic peaks of WO_3 crystals were detected at 23.12°, 23.60°, and 24.38° (Fig. 1). As expected [27–29], the intensity of the WO_3 peaks increased with WO_3 loading. Figure 2 shows the XRD patterns of the NaOH-treated catalysts compared with the pristine catalysts with different tungsten loading. The intensity of the XRD peaks decreased after the NaOH treatment. A sharp decrease in the intensity of the WO_3 crystal peaks was observed for modified 4%WO_3/SiO_2. In contrast, only small changes were observed for the catalysts with higher tungsten loading. The XRD results were in good agreement with the ICP-OES results that the NaOH ion exchange led to a significant loss of WO_3 species only with the 4%WO_3/SiO_2 catalyst.

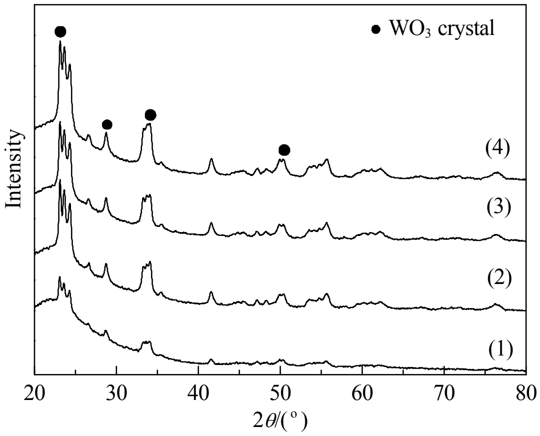

Fig. 1. XRD patterns of pristine catalysts with different tungsten loading. (1) 4%WO_3/SiO_2; (2) 6%WO_3/SiO_2; (3) 8%WO_3/SiO_2; (4) 10%WO_3/SiO_2.

Raman spectroscopy was used to determine the structure of the tungsten species present on the supported catalysts (Fig. 3). The Raman bands at 498, 602, 808, and 1060 cm^{-1} were assigned to the characteristic vibrations of four- and three-member silica rings and Si–O–Si stretching, respectively [30]. As expected from the XRD results, the Raman bands of crystalline WO_3 were observed for all the pristine catalysts. The bands at 263–275, 707–720, and 807–808 cm^{-1} were assigned to the deformation mode of W–O–W, bending mode of W–O, and symmetric stretching mode of W–O, respectively [28]. The broad band at 970 cm^{-1} was assigned to the O=W=O band of isolated surface tetrahedral tungsten oxide species [31], which was reported as the active species for metathesis [17]. As reported by Andreini et al. [18] and Debecker et al. [10], the active tungsten compound was difficult to reduce whereas the crystalline WO_3 can be reduced easily, implying that the tetrahedral tungsten oxide species has a stronger interaction with the support than does the crystalline WO_3. In the present work, the catalysts exhibited different intensity for the bands at 710,

Table 1

Measured composition of WO_3, textural characterization, and total acidity (ion exchange titration) of the pristine catalysts and modified catalysts.

Catalyst	Actual WO_3 composition (wt%)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Total acidity (μmol H^+/g-catalyst)
4%WO_3/SiO_2	3.68	281	0.98	9.32	74
4W+0.5NaOH	1.17	283	0.99	9.38	61
4W+1.0NaOH	1.10	285	0.99	9.37	51
4W+1.5NaOH	0.94	288	1.01	9.38	40
6%WO_3/SiO_2	5.05	278	0.95	9.29	83
6W+1.0NaOH	4.60	279	0.95	9.29	58
6W+1.5NaOH	4.03	280	0.97	9.32	35
8%WO_3/SiO_2	7.02	277	0.92	9.28	95
8W+1.0NaOH	6.58	280	0.94	9.29	67
8W+1.5NaOH	6.08	279	0.95	9.31	42
10%WO_3/SiO_2	9.14	269	0.87	9.27	101
10W+0.5NaOH	8.82	269	0.88	9.25	82
10W+1.0NaOH	8.68	271	0.88	9.27	65
10W+1.5NaOH	8.25	273	0.90	9.26	46

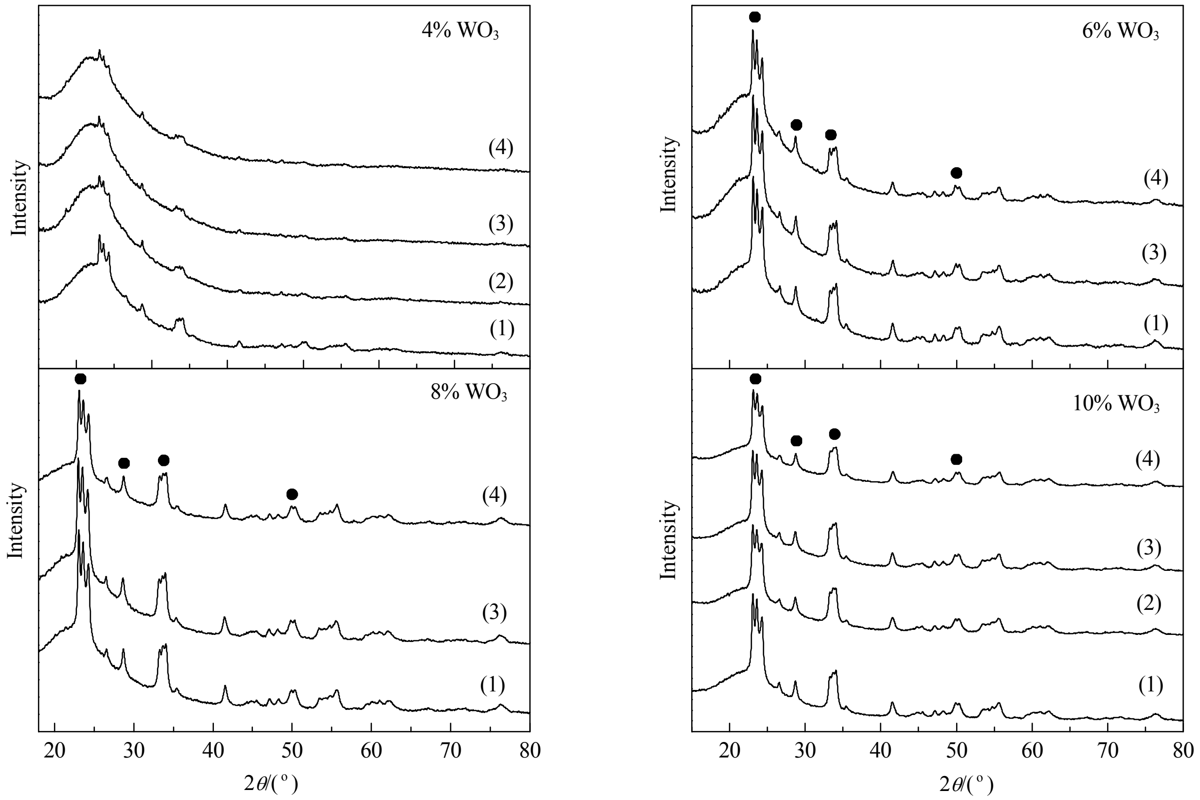

Fig. 2. XRD patterns of pristine catalysts compared with modified catalysts with different tungsten loading. (1) Pristine catalyst; (2) Modified with 0.5NaOH; (3) Modified with 1.0NaOH; (4) Modified with 1.5NaOH.

807, and 970 cm^{-1}. When the tungsten loading was increased, sharp increases in the intensity were observed at the 710 and 807 cm^{-1} bands (crystalline species), while there was only a slight increase in the band at 970 cm^{-1} (isolated species) with the maximum intensity for 8% WO_3 loading.

The same WO_x species was observed on all the NaOH-treated catalysts (Fig. 4). The spectrum of the 4%WO_3/SiO_2 catalyst was significantly modified. The intensity of the bands corresponding to the crystalline species (710 and 807 cm^{-1}) was decreased drastically, as was the band corresponding to the isolated species (970 cm^{-1}). This effect was larger when the concentration of NaOH was increased. For the catalyst with higher loading, the effect of NaOH treatment was not very pronounced. Only the bands corresponding to the crystalline WO_3 species were progressively smaller, while the band corresponding to the isolated species was hardly affected.

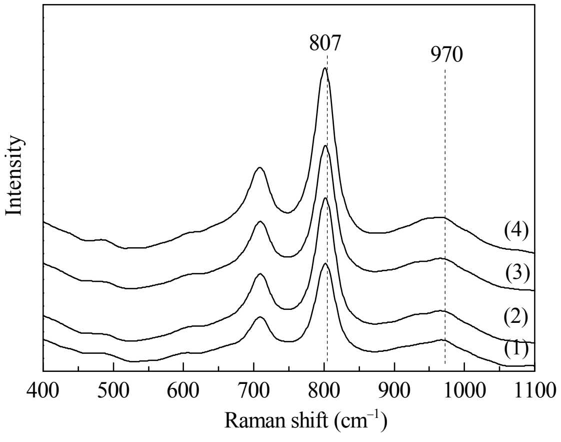

Fig. 3. Raman spectra of the pristine catalysts with different tungsten loading. (1) 4%WO_3/SiO_2; (2) 6%WO_3/SiO_2; (3) 8%WO_3/SiO_2; (4) 10%WO_3/SiO_2.

Thus the ICP-OES data, XRD data, and Raman spectroscopy consistently indicated that: (i) 4%WO_3/SiO_2 was strongly affected by the NaOH treatment, (ii) catalysts with higher loading were only slightly affected, and (iii) the main effect was that part of the crystalline species present on the catalysts was leached off.

The NH_3-TPD experiments demonstrated the effect of the NaOH treatment on the acidity of the catalysts (Fig. 5). Because the silica support is not acidic [18], the acid sites were due to the tungsten oxide. The low temperature peak of the pristine catalysts at 110–130 °C corresponded to weak acid sites [28]. The acidity of the pristine catalysts increased with increasing tungsten loading, which is in good agreement with the literature [29]. Both titration (Table 1) and NH_3-TPD data agreed in showing that the acidity was decreased after the treatment with NaOH. It is interesting to note that the low temperature peak of the modified catalysts was shifted to a higher temperature. Thus, while poisoning appears to affect both types of acidic sites, it must be noticed that part of the stronger sites remained on the catalyst.

In order to gain further insight into the roles of the Lewis

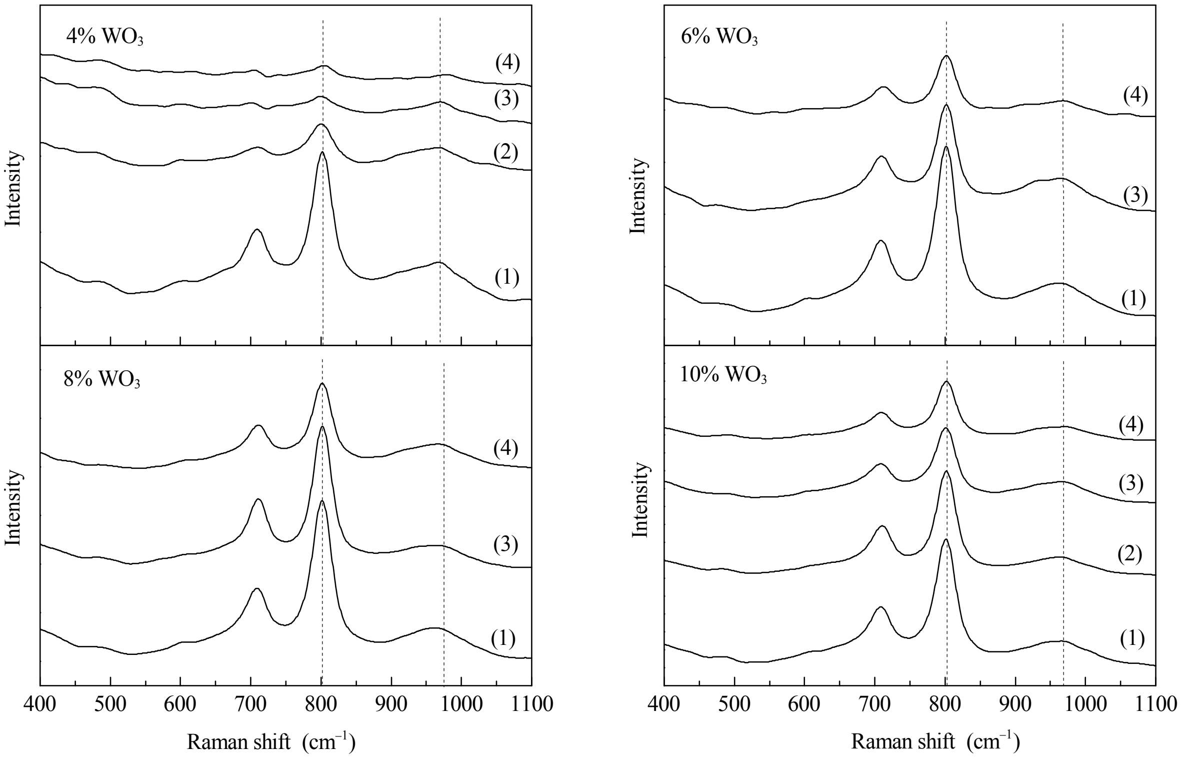

Fig. 4. Raman spectra of the pristine catalysts compared to the modified catalysts with different tungsten loading. (1) Pristine catalyst; (2) Modified with 0.5NaOH; (3) Modified with 1.0NaOH; (4) Modified with 1.5NaOH.

and Brönsted acid sites on these metathesis catalysts, a study was performed by infrared spectroscopy of pyridine adsorption (Fig. 6). The peak at 1596 cm^{-1} was due to hydrogen bonded pyridine. The peaks at 1623, 1575, and 1445 cm^{-1} corresponded to Lewis acid sites. Brönsted acid sites were shown by the peaks at 1545 and 1639 cm^{-1}. The peak at 1492 cm^{-1} was attributed to pyridine adsorbed on both Brönsted and Lewis acid sites [32,33]. Figure 6 shows that the Lewis acid sites increased markedly with increasing WO_3 loading, which was in agreement with the literature [29,34]. The Brönsted acidity peaks, however, were very weak. Tiny peaks were seen at 1545 and 1639 cm^{-1} with the catalysts with 8% and 10% WO_3 loading. Thus Brönsted sites were either not abundant or relatively weak on these catalysts. This is consistent with previous reports showing that significant Brönsted acidity was only generated on catalysts with high WO_3 contents [34].

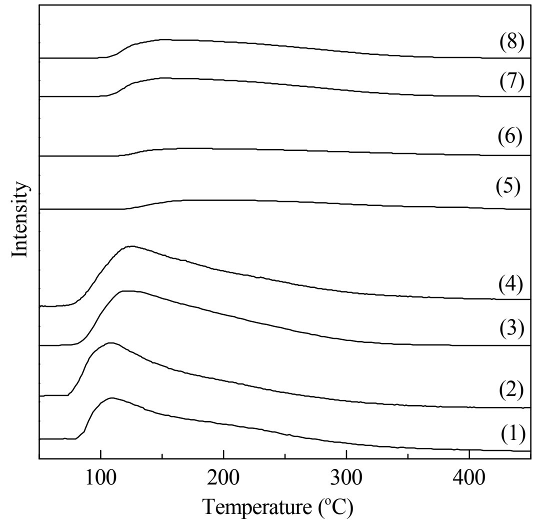

Fig. 5. NH_3-TPD profiles of the pristine catalysts compared with the modified catalysts with different tungsten loading. (1) 4%WO_3/SiO_2; (2) 6%WO_3/SiO_2; (3) 8%WO_3/SiO_2; (4) 10%WO_3/SiO_2; (5) 4W+1.5NaOH; (6) 6W+1.5NaOH; (7) 8W+1.5NaOH; (8) 10W+1.5NaOH.

Figure 7 shows the FT-IR pyridine spectra of the NaOH-treated catalysts as compared to the pristine catalysts. The signals corresponding to the Brönsted sites were now totally

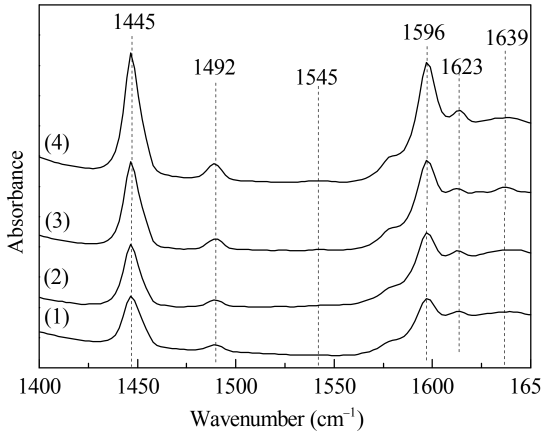

Fig. 6. FT-IR spectra of pyridine adsorbed at 50 °C on catalysts with different tungsten loading. (1) 4%WO_3/SiO_2; (2) 6%WO_3/SiO_2; (3) 8%WO_3/SiO_2; (4) 10%WO_3/SiO_2.

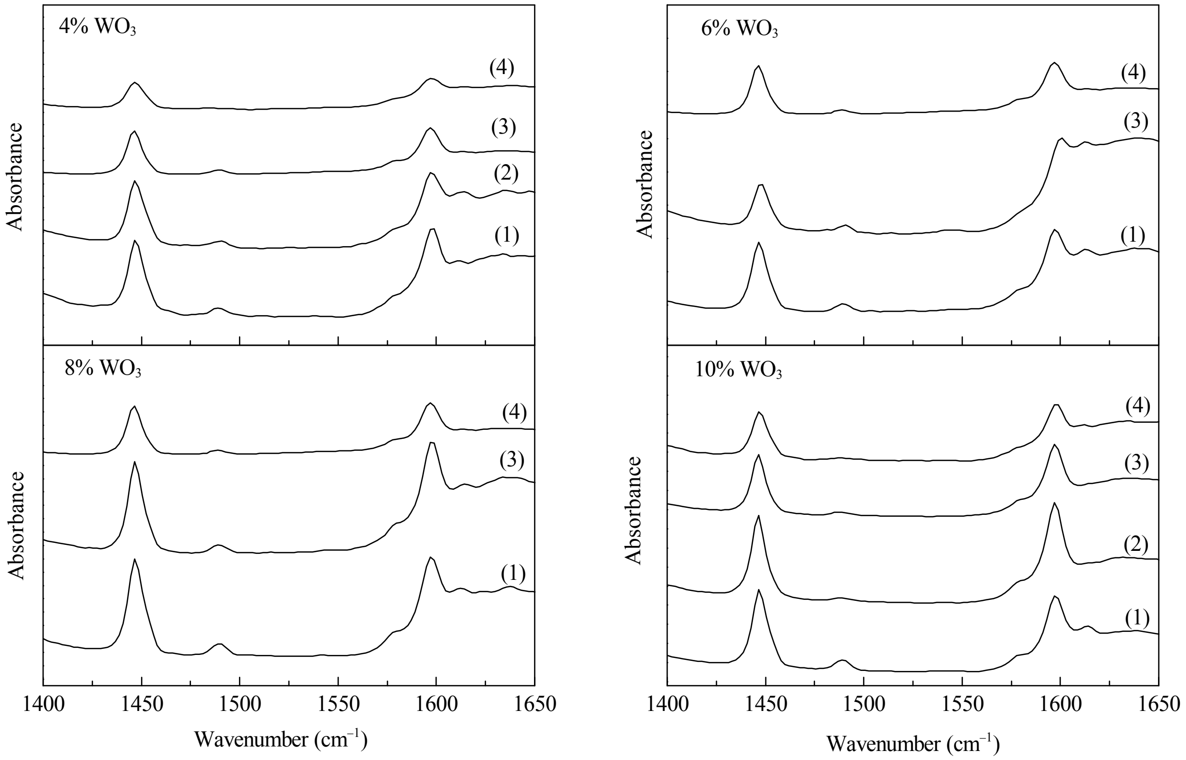

Fig. 7. FT-IR spectra of pyridine adsorbed at 50 °C on pristine catalysts compared with modified catalysts with different tungsten loading. (1) Pristine catalyst; (2) Modified with 0.5NaOH; (3) Modified with 1.0NaOH; (4) Modified with 1.5NaOH.

absent, even for the catalysts with the highest loading. For the Lewis sites, it was clear that the ion exchange with NaOH had a marked effect. In particular, the intensity of the peak at 1455 cm^{-1} was progressively reduced as the NaOH solution used for ion exchange was more concentrated. The intensity of the peak at 1492 cm^{-1} (which represented both Brönsted and Lewis sites) also decreased after NaOH treatment.

By correlating the results of FT-IR-pyridine with the NH_3-TPD results, it can be concluded that the treatment with NaOH resulted in a progressive decrease in total acidity. The remaining acidity was attributed to Lewis acid sites with a strong interaction with the silica support.

3.2. *Metathesis activity and selectivity*

The metathesis activity of different WO_3/SiO_2 catalysts was evaluated at 400 °C for 10 h. The results are shown in Fig. 8. Metathesis activity, expressed by the conversion of *trans*-2-butene, increased with increasing tungsten loading and reached a maximum of 80% conversion with 8%WO_3/SiO_2. Further increasing of the tungsten loading to 10%WO_3/SiO_2 did not result in a further performance increase. It is widely accepted that dispersed tetrahedral tungsten oxide species are the active sites for the metathesis reaction [11,17,27]. Here, Raman results indicated a relatively high proportion of tetra-

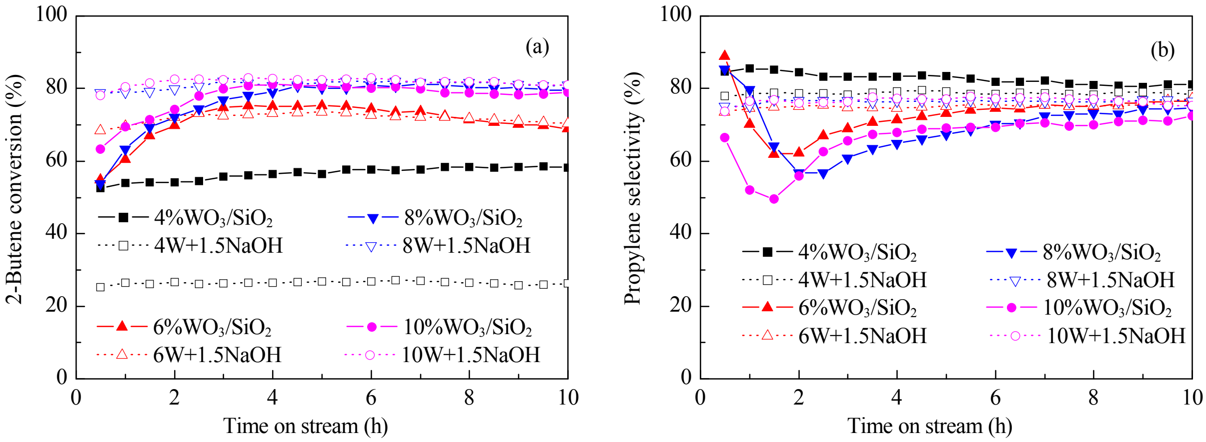

Fig. 8. 2-Butene conversion (a) and propylene selectivity (b) over different catalysts.

hedral tungsten oxide species (band at 970 cm^{-1}) on the most active catalyst (8%WO_3).

After the treatment with NaOH, the metathesis activity was significantly decreased only for the 4%WO_3/SiO_2 catalyst. However, one cannot draw definitive conclusions because other parameters were changed as well. In particular, the tungsten loading was dramatically decreased (by leaching). Interestingly, the metathesis activity of the modified catalysts with higher tungsten loading (6%–10%) remained almost unchanged after the NaOH treatment. Thus the small proportion of the WO_x species that were leached from these catalysts (at most 15% of the original WO_3, and most probably these were mainly crystalline WO_3) were species that were not active in the metathesis reaction. In other words, the active species, isolated tetrahedral species with a strong interaction with the support, remained on the catalyst after NaOH treatment. This was also suggested by the H_2-TPR data (not shown in this paper) where the reduction peak was slightly decreased and shifted to a higher temperature with the treated catalysts. However, on these NaOH-treated catalysts, the acidity was significantly modified as compared to the pristine catalysts. The fact that the activity remained at the same level showed that the acidity of these treated catalyst was still sufficient to generate active metathesis sites and for the metathesis reaction to occur.

As can be seen in Fig. 9, after pretreatment with NaOH, the total acidity (measured by liquid phase titration) and Lewis acidity (evaluated by FT-IR of pyridine adsorption) decreased progressively when higher concentrations of NaOH were used for the ion exchange. At the highest concentration of NaOH used, the Lewis acidity was decreased by about 50% (evaluated by the decrease of the FT-IR peak intensity). It should be pointed out that Lewis acid sites were shown to be necessary for the formation of the initial metal carbene species for the metathesis reaction [13,18]. Here, although the Lewis acidity was decreased by the NaOH treatment, the metathesis activity remained unchanged. This suggested that even with the catalysts with the lowest acidity, the Lewis acidity was still enough to convert the reactant olefins.

Table 2 summarizes the selectivity to propylene and the other products of the reaction. The propylene selectivity over the pristine catalysts decreased from 81.1% to 72.4% when the tungsten loading was increased from 4% to 10%. The highest propylene selectivity was obtained over 4%WO_3/SiO_2, which was due probably to the higher dispersion of tungsten and the lower proportion of WO_3 crystals. Interestingly, after treatment with NaOH, propene selectivity increased for all the catalysts except 4%WO_3/SiO_2. At the same time, selectivity to isomerization products (1-butene, *cis*-2-butene) slightly decreased. Thus the desired metathesis reaction was slightly favored over the undesired side reactions. This was attributed to the removal of residual Brönsted acidity on the NaOH-treated catalysts. However, this was difficult to demonstrate because the FT-IR spectroscopy of adsorbed pyridine was not sensitive enough to probe quantitatively the weak or scarce Brönsted acid sites. Compared with Spamer et al. [20] who aimed to reduce the occurrence of isomerization in the liquid phase metathesis of 1-octene, the observed effect of alkaline doping here was modest. Nevertheless, the propylene yields increased from 52.7% to 55.3%, from 59% to 63.0%, and from 57.2% to 61.2% when NaOH ion exchange was applied to the 6%, 8%, and 10% loaded catalysts, respectively. Thus, when W leaching is not too pronounced, NaOH ion exchange appears to be a good way to

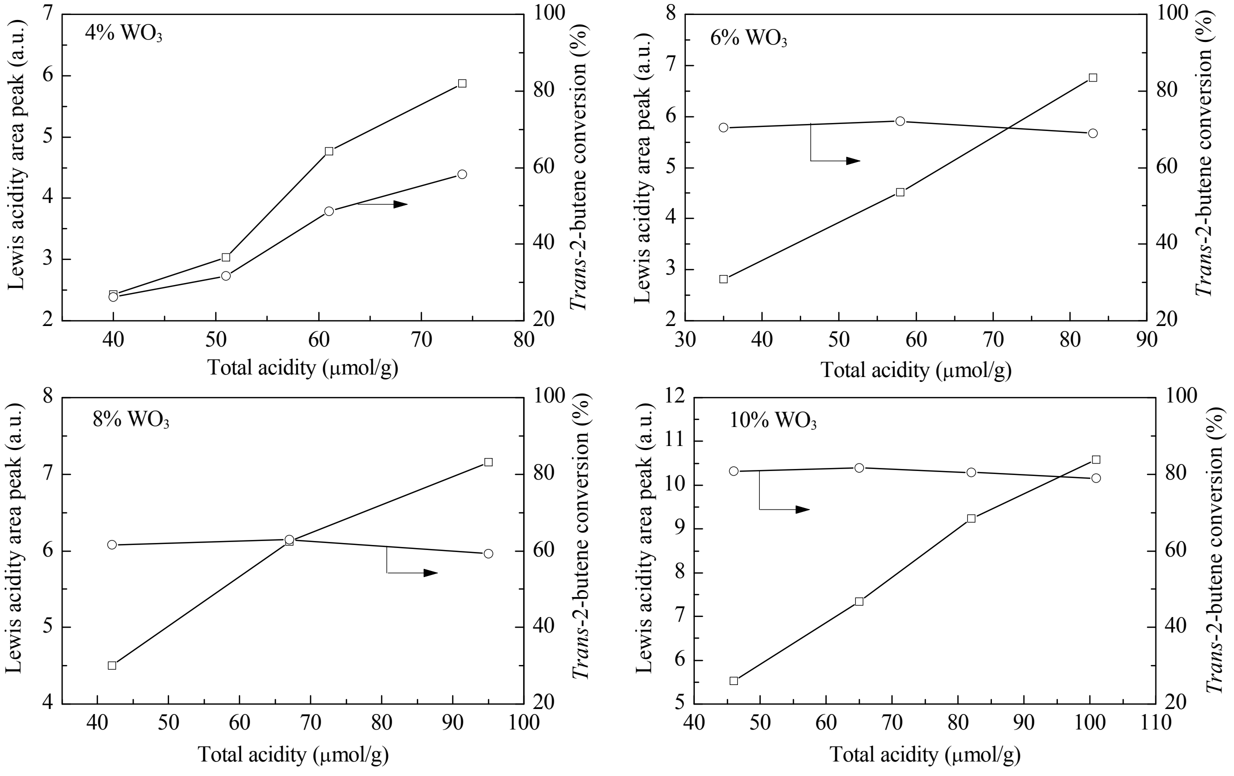

Fig. 9. Correlation between total acidity, Lewis acidity, and *trans*-2-butene conversion.

Table 2
Activity of pristine catalysts and modified catalysts with different tungsten loading.

Catalyst	Conversion of *trans*-2-butene (%)	Selectivity (%)					Yield of propylene (%)
		Propylene	1-Butene	1,3-Butadiene	*Cis*-2-butene	Others	
4%WO_3/SiO_2	58.2	81.1	8.2	0	9.4	1.3	47.2
4W+0.5NaOH	48.6	64.0	17.8	0	16.1	2.1	31.1
4W+1.0NaOH	31.7	67.2	16.5	0	14.4	1.9	21.3
4W+1.5NaOH	26.2	78.5	10.2	0	8.8	2.5	20.6
6%WO_3/SiO_2	68.9	76.5	10.5	0.2	10.6	2.2	52.7
6W+1.0NaOH	72.1	76.7	11.0	0.2	9.8	2.3	55.3
6W+1.5NaOH	70.4	77.2	10.6	0.1	10.0	2.1	54.3
8%WO_3/SiO_2	79.3	74.6	10.8	0.4	11.5	2.7	59.2
8W+1.0NaOH	81.2	77.6	10.1	0.3	9.5	2.6	63.0
8W+1.5NaOH	80.4	76.6	9.9	0.3	10.4	2.8	61.6
10%WO_3/SiO_2	79.0	72.4	12.1	0.5	12.0	3.0	57.2
10W+0.5NaOH	80.4	73.6	11.8	0.4	11.4	2.9	59.2
10W+1.0NaOH	81.6	75.0	10.7	0.3	11.1	2.9	61.2
10W+1.5NaOH	80.8	75.3	10.9	0.3	10.7	2.8	60.8

All reactions were online for 10 h. Reaction conditions were 400 °C and 0.1 MPa.

increase the propene yield a little bit more.

The metathesis reaction mechanism includes the formation of a surface carbene by the reaction of tungsten oxo species with the olefins in the feed. The stability of WO_x surface species and their tendency to react with the olefins is also dictated by the structure of the surface tungsten oxide species [15]. Well dispersed tetrahedral tungsten species react better with the olefins to yield the desired carbene species [11,13,35]. On comparing the catalytic performance of the pristine catalysts (Fig. 8), 4%WO_3/SiO_2 reached modest activity after a relatively short induction period. Catalysts with higher loading (6%–10%) had a longer induction period, suggesting that the formation of the carbene species is facilitated when the dispersion is higher. More important was that the NaOH-treated catalysts reached the steady state much faster than did the pristine catalysts (Fig. 8). This was correlated with that the dispersion of tungsten in the form of tetrahedral species was favored by the NaOH treatment.

Figure 10 depicts the effect of NaOH treatment on the stability of the catalyst in the first stage of the reaction and also shows catalyst stability over a longer reaction run (30 h). Both the pristine catalyst and modified catalyst reached stable conversion and selectivity and did not show deactivation in the time frame of our experiment. However, this stable behavior was only reached after an induction period of about 10 h with the pristine catalyst while it is almost immediately reached with the modified catalyst as described above.

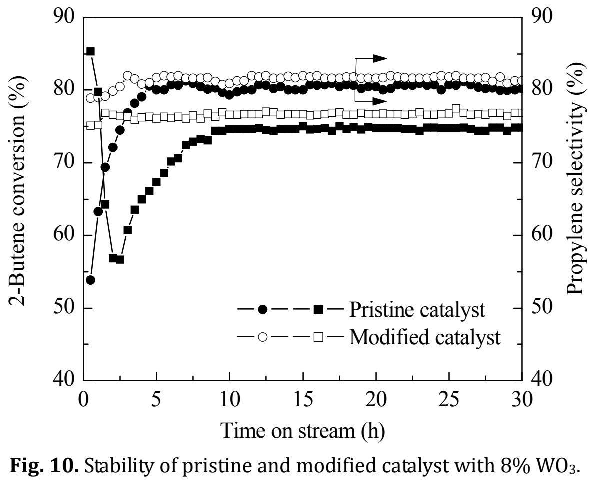

Fig. 10. Stability of pristine and modified catalyst with 8% WO_3.

TGA analysis was used for determining coke formation on the spent catalysts compared to the pristine catalysts and modified catalysts. Coke on oxide catalysts is thought to arise from alkene polymerization, alkene cyclization, and polyaromatic formation [23]. These reactions are catalyzed by acidic sites, especially Brönsted acid sites [23,24]. Coke formation can be reduced by adding promoters, which can partially eliminate acidic sites [25], or by an acid leaching post-treatment [22]. In the present work, the effect of coke formation after the treatment with NaOH was also studied. After 10 h metathesis reaction at 400 °C, the temperature was decreased to room temperature and then a nitrogen flow was admitted. Table 3 shows that the coke contents on all samples were quite low as compared to the long run experiments reported in the literature [21]. The result also showed clearly that the coke content on the modified catalyst was lower than that on the pristine catalyst. This was also seen with the TGA and DTG profiles (not shown here). The DTG of both coked catalysts showed a similar pattern of mass loss. Two mass loss peaks were observed at 280 and 460 °C, which corresponded to aliphatic hydrocarbons (soft coke) and polyaromatics (hard coke), respectively [36,37].

Table 3
Coked WO_3/SiO_2 catalysts for comparing the coke content on the pristine and modified catalysts.

Catalyst	Coke (%)
6%WO_3/SiO_2	0.14
6W+1.5NaOH	0.06
8%WO_3/SiO_2	0.16
8W+1.5NaOH	0.08
10%WO_3/SiO_2	0.22
10W+1.5NaOH	0.11

The intensity of both mass loss peaks decreased after the treatment with NaOH, indicating that the acidity that is responsible for coke formation was reduced. Thus the benefits of acid site poisoning also included a prolonged lifetime of the catalyst. Note that coke formation did not result in any significant modification of the catalyst texture (data not shown). Moodley et al. [21] used EFTEM to determine the location of the coke on the WO_3/SiO_2 catalyst and suggested that the coke laydown rather than the amount of coke was decisive in determining the activity. In the present study, the activity of the modified catalyst was maintained at the same level for 30 h, indicating good stability, as compared to a previous report [8]. Nevertheless, coke formation during prolonged catalytic reaction should be further investigated.

In summary, Na doping did not affect significantly the metathesis activity of WO_3/SiO_2 catalysts but reduced slightly their isomerization activity. As a result, NaOH ion exchange is a good way to increase propylene yield. The effect of this treatment was beneficial both in helping the catalyst reach the steady state in a shorter time and minimizing coke deposition, which increased the lifetime of the WO_3/SiO_2 catalyst.

4. Conclusions

Ion exchange with NaOH was used to mitigate the acidity of WO_3/SiO_2 metathesis catalysts. This treatment had a large effect on the catalyst with a low WO_3 loading, esp. in causing a marked leaching of the W species. On the catalysts with 6% WO_3 to 10% WO_3, the ion exchange mainly had an effect on the acidity. Although both Lewis and Brönsted acid sites were decreased, the metathesis acidity remained the same. This indicated that the acid sites on the NaOH-treated catalysts were still enough for the active species to form. However, the isomerization activity was slightly decreased by the NaOH treatment. Thus NaOH treatment is a good way to tune the selectivity of WO_3/SiO_2 catalysts to give a little more propene yield without affecting their metathesis activity. Other beneficial effects of the NaOH treatment were to shorten the induction period and to decrease deactivation by coke formation.

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Graphical Abstract

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NaOH modified WO_3/SiO_2 catalysts for propylene production from 2-butene and ethylene metathesis

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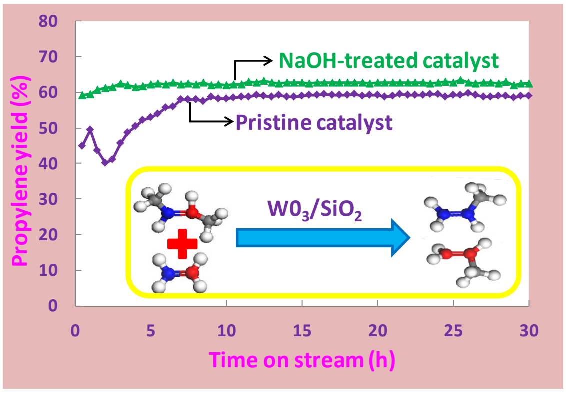

After treatment of a WO_3/SiO_2 catalyst with NaOH to reduce its acidity, the conversion was not changed but isomerization was slightly reduced, and the final propene yield and overall catalyst stability were improved.

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