Catalysis Letters Vol. 92, Nos. 3–4, February 2004 (© 2004)

Characterization and catalytic behavior of potassium-modified ZrO_2 base catalysts

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Received 5 August 2003; accepted 17 November 2003

Potassium-modified ZrO_2 base catalysts were prepared by wet impregnation of hydrous zirconia and anhydrous zirconia with potassium compounds and calcined at 600 °C in air. The properties of the catalysts were characterized and compared. Catalytic activities were examined for the vapor-phase double-bond isomerization of 1-butene at 150 °C and the liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone at room temperature. The properties of the modified ZrO_2 i.e., basic site strength, were greatly affected by the ZrO_2 precursors and the potassium modifiers. High yields of 2-butene with relatively high cis/trans ratios were found. Leaching of the potassium-modified ZrO_2 makes the system less suitable for use in liquid-phase reactions.

KEY WORDS: potassium-modified ZrO_2; base catalysts; isomerization of 1-butene; Michael addition.

1. Introduction

ZrO_2 has attracted more and more attention as a promising catalyst and catalyst support because of its high thermal stability, amphoteric nature, and redox properties [1]. Until now, ZrO_2 has been transformed into strong, solid acid catalysts by modification with sulfate [2–7], WO_3 [8], MoO_3 [9], or B_2O_3 [10,11]. These ZrO_2-based solid acid catalysts show high activity and selectivity in many reactions [2–11]. However, few efforts have been made to turn ZrO_2 into a base catalyst by taking advantage of its natural basicity, although several studies have been done on a highly effective alkali-modified ZrO_2 catalyst for the oxidative coupling of methane [12,13]. In general, it is common to prepare base catalysts by modifying or supporting alkali metal oxides on various supports [14]. Various alkali metal oxides have been loaded on different supports, such as magnesium oxide [15], zeolites [16–19], alumina [19–21], and silica [22], by the decomposition of alkali compounds. These catalysts have proved to be excellent solid-base catalysts for numerous vapor-phase probe reactions, such as isopropanol dehydrogenation [16,19,22], the isomerization of 1-butene [17,23,24] and *cis*-but-2-ene [25], the methylation of phenol [22], toluene [26], and catechol [27] with methanol. However, alkali metal oxides–supported catalysts used in liquid-phase, base-catalyzed reactions have been investigated less. It is not clear whether this kind of catalyst is a real heterogeneous catalyst in liquid-phase reactions. Recently, Wang *et al.* [25] used a dry impregnation process to prepare KNO_3/ZrO_2 superbases, which possessed a base strength of $H_- = 27.0$ and were very active for *cis*-but-2-ene isomerization under mild conditions. Here, we report on the properties of potassium-modified ZrO_2 prepared by the calcination of hydrous zirconia and anhydrous zirconia after impregnation with potassium compounds. The catalytic activity of this system was studied in the vapor-phase isomerization of 1-butene and in the liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone.

2. Experimental

2.1. Catalyst preparation

Hydrous zirconia, $ZrO(OH)_2 \cdot aq$, was prepared from $ZrOCl_2 \cdot 8H_2O$ (Fluka, 99%) according to Parida *et al.* [28]. Pure anhydrous ZrO_2 was obtained by calcination of hydrous zirconia at 600 °C in air for 4 h. The supported catalysts were prepared by wet impregnation of $ZrO(OH)_2$ (ZRH samples) and ZrO_2 (ZRO samples) powders with aqueous solutions of $KHCO_3$, K_2CO_3, KOAc, and KNO_3 (in most cases, about 1.0 mL solution for 1.0 g powder). The theoretical K/Zr ratios were 0.2. After impregnation, the excess solution was evaporated at room temperature. The samples were then dried at 110 °C (for the samples modified with $KHCO_3$, 80 °C was used instead), calcined at 600 °C in flowing air for 4 h, and stored in closed containers until used.

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2.2. Characterization

2.2.1. XRD and textural properties

Identification of the samples was performed using X-ray powder diffraction with Cu Kα radiation (XRD 7, Rich. Seifert & Co., Freiberg). The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 system after the calcined samples were degassed at 200 °C overnight. Surface areas were calculated using the BET method. Pore volumes and pore distributions were calculated using the BJH method. The contents of carbon, hydrogen, and nitrogen were determined by elemental analysis. Potassium and zirconium contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2.2. TG-DTG-DTA

Thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis measurements (DTA) were performed using a NETZSCH STA409C system equipped with a skimmer-coupled mass spectrometer in airflow, with a heating rate of 10 °C/ min up to 700 °C, and Al_2O_3 as a reference.

2.2.3. CO_2-TPD

CO_2-TPD was used to measure the strength of basic sites. The pelleted sample (approximately 300 mg, 0.3–0.5-mm diameter fraction) was pretreated in a nickel reactor under Ar (70 mL/min) at 600 °C for 1 h. The sample was then cooled to 50 °C and exposed to a stream of Ar and CO_2. The sample was flushed for over 1 h at 50 °C to remove physisorbed CO_2, after which the TPD program (10 °C/ min, up to 600 °C, held for 30 min) was started. The desorption of gas-phase CO_2 was detected by monitoring the band at 2349 cm^{-} with FTIR spectroscopy (FTIR system 2000, Perkin–Elmer).

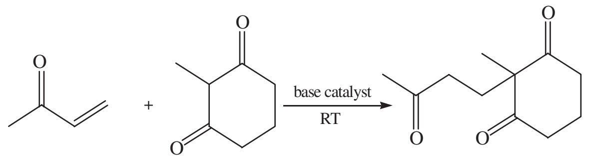
2.3. Catalytic screening procedure

2.3.1. Vapor-phase reaction: double-bond isomerization of 1-butene

The isomerization of 1-butene was performed in a down-flow, fixed-bed glass reactor. Equal volumes of the pelleted, calcined catalyst (about 300–450 mg, 0.3–0.5 mm diameter fraction) were exposed to the feed stream mixture of nitrogen (10 mL/min) and 1-butene (0.6 mL/min) at 150 °C. Prior to the reaction, the catalyst was pretreated in N_2 at 600 °C for 2 h. On-line gas chromatography (Shimadzu GC-17A, FID, quartz capillary: PONA (methylsiloxane), 50 m, 0.2 mm × 0.5μm) was used to determine the composition of the reaction mixture of 1-butene and *cis/trans*-2-butene after a time onstream (TOS) of 10, 30, 60, and 90 min. Owing to 100% product selectivity, the reaction conversion is given by the yield of 2-butene product. Product yields were normalized by the mass of the catalyst used at 30 min in order to compare the catalysts' results with each other.

2.3.2. Liquid-phase Michael addition

The Michael addition is given in scheme 1. The reaction was carried out in a 50-mL round-bottomed flask at room temperature. Methyl vinyl ketone (22.5 mmol, Aldrich, 99%), 2-methylcyclohexane-1,3-dione (15.0 mmol, Acros, 98%), dimethyl phthalate (3.75 mmol, Acros, 99%, internal standard for monitoring the product formation), and the solvent methanol (10 mL, Aldrich, 99%) were stirred for 30 min to saturate the mixture with 2-methylcyclohexane-1,3-dione (which is only slightly soluble in methanol), before the powdered solid catalyst (0.225 g) was added. Samples of the reaction slurry (about 0.3 mL) were collected after a specific amount of time, centrifuged, and concentrated on a rotary evaporator to remove the solvent and unreacted methyl vinyl ketone. The yield of the target product was analyzed by ^1H NMR spectroscopy (solvent: DMSO-d_6) using the integrals of the CH_3-signals of 2-(γ-oxobutyl)-2-methylcyclohexane-1,3-dione (1.11 and 2.04 ppm) and dimethyl phthalate (3.83 ppm).



Methyl vinyl ketone 2-Methylcyclohexane-1.3-dione 2-(Oxobutyl)-2-methylcyclohexane-1.3-dione

Scheme 1

3. Results and discussion

Table 1 gives the notations and characteristics of the samples. Figure 1 shows the XRD patterns of some samples after calcination. Amorphous, hydrous zirconia formed monoclinic ZrO_2 after calcination at 600 °C (figure 1(a)). However, after the modification of hydrous zirconia using C-containing potassium compounds mentioned above and calcination, the main phase of KC-ZRH, KHC-ZRH, and KAC-ZRH (figure 1(b)) was metastable, tetragonal ZrO_2. Both the tetragonal and monoclinic phase were found in KN-ZRH (figure 1(c)). It has been postulated that the K^+ ions are incorporated in the vacant sites on the surface of hydrous zirconia and stabilize the tetragonal ZrO_2 phase [25,29]. All of the ZRH samples, except for KN-ZRH, also have sharper and more intense XRD peaks than those of the pure ZrO_2 and the ZRO samples; this indicates higher sample crystallinity of the ZRH samples. Almost no phase or intensity change was found in the XRD patterns of the impregnated,

Table 1
Characteristics of different potassium-modified zirconia catalysts

Sample	Precursor	Modifying agent	XRD		S_{BET} (m^2/g)	V_P[a] (cm^3/g)	d_p[b] (Å)	X-content (wt%)[c]		K/Zr (mol)[d]
			bc	ac				bc	ac	
ZR	$ZrO(OH)_2$	–	A	M	26.0	0.08	127	C:0.23,H:1.19	C:0.04,H:0.08	–
KC-ZRH	$ZrO(OH)_2$	K_2CO_3	A	T+M	7.4	0.04	212	C:1.23,H:1.28	C:0.45,H:0.13	0.18
KHC-ZRH	$ZrO(OH)_2$	$KHCO_3$	A	T+M	6.3	0.03	281	C:1.19,H:1.33	C:0.46,H:0.14	0.19
KAC-ZRH	$ZrO(OH)_2$	KOAc	A	T+M	9.5	0.04	185	C:3.45,H:1.33	C:0.51,H:0.10	0.17
KN-ZRH	$ZrO(OH)_2$	KNO_3	A	M+T	4.8	0.04	322	C:0.37,H:1.14,N:2.21	C:0.26,H:0.06,N:1.00	0.18
KC-ZRO	ZrO_2	K_2CO_3	M	M	10.0	0.06	219	C:1.01,H:0.12	C:0.80,H:0.12	0.15
KHC-ZRO	ZrO_2	$KHCO_3$	M	M	11.7	0.07	236	C:1.30,H:0.22	C:0.72,H:0.16	0.16
KAC-ZRO	ZrO_2	KOAc	M	M	11.1	0.06	220	C:3.00,H:0.52	C:0.87,H:0.11	0.14
KN-ZRO	ZrO_2	KNO_3	M	M	3.0	0.02	266	C:0.14,H:0.10,N:2.57	C:0.13,H:0.09,N:1.61	0.17

Note: bc: before calcination, ac: after calcination at 600 °C, A: amorphous zirconia, M: monoclinic zirconia (PDF-No.78-47), T: tetragonal zirconia (PDF-No.80-784), T+M: tetragonal zirconia was the main phase, M+T: coexistence of the tetragonal and monoclinic phases.[a]BJH desorption cumulative pore volume of pores between 17.0 and 3000.0 Å diameter.

[b]Average pore diameter by BET.

[c]Element analysis.

[d]ICP-OES results of calcined samples.

anhydrous ZrO_2 samples after modification with potassium compounds (figure 1(d), KAC-ZRO).

The adsorption/desorption isotherms of all the samples are of type IV. The hysteresis loops, owing to the capillary condensation associated with large mesopores, can be ascribed to the H2 Type [30]. There is not much difference between the adsorption/desorption isotherms of pure ZrO_2 and modified ZrO_2, but the specific surface areas of the modified samples are much lower than that of ZrO_2, whereas the pore volumes are only slightly smaller (table 1). The decrease in surface area may be attributed to: (1) rearrangements during the formation of the networks, (2) surface covering by potassium oxide produced at higher temperatures, or (3) the presence of bulk potassium compounds on the surface. On the other hand, the average pore diameters of the samples were somewhat larger (table 1). The mesopore-size distributions of some samples are shown in figure 2. The curves all show sharp maxima with narrow distributions. The pore diameters of pure anhydrous ZrO_2 and the modified samples were centered at about 70 and 100–180 Å respectively (figure 2). Except for the KNO_3-modified samples with the lowest pore volume, the anhydrous ZrO_2-supported samples (KC-ZRO, KHC-ZRO, and KAC-ZRO) had pores with higher pore volumes than that of the hydrous ZrO_2-supported samples, KC-ZRH, KHC-ZRH, and KAC-ZRH. The carbon and nitrogen contents of the calcined samples indicate that the potassium compounds

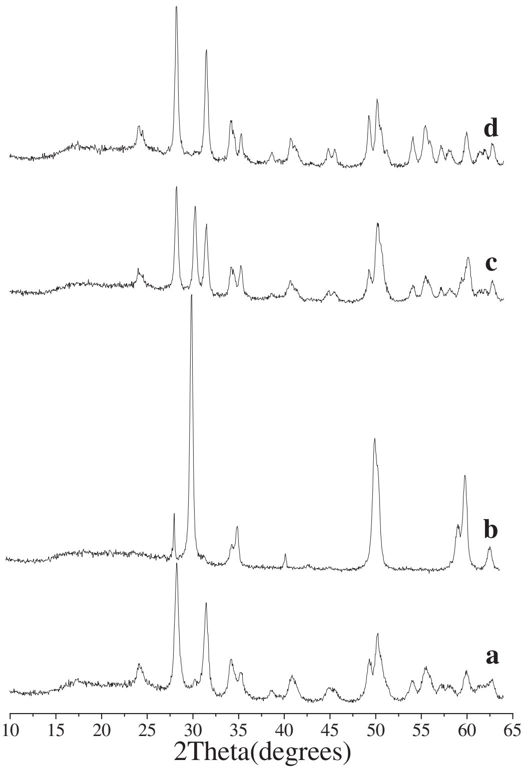


Figure 1. XRD patterns of the catalysts after calcinations: (a) ZR; (b) KAC-ZRH; (c) KN-ZRH; (d) KAC-ZRO.

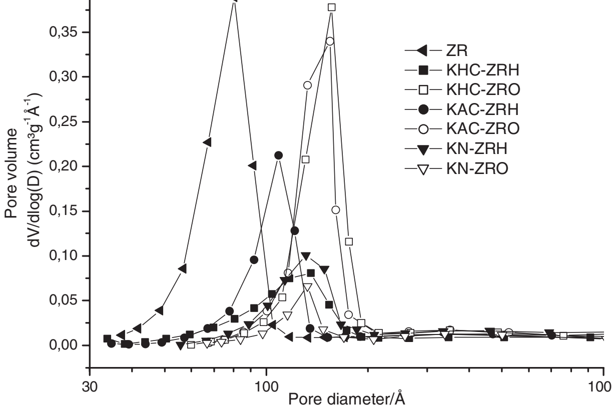


Figure 2. Pore-size distributions of the indicated catalysts.

have not decomposed completely, which may be one reason for the decrease in surface area. The K/Zr mole ratios of calcined samples measured by ICP-OES were close to the nominal value of 0.2 (table 1).

TG-DTG-DTA was used to investigate the decomposition of potassium compounds on ZrO_2.

The profiles of KHC-ZRH and KHC-ZRO are shown in figure 3. From the profiles of KHC-ZRH, a broad endothermic effect, two DTG peaks, and 13% weight loss were observed from 100 to 400 °C, which can be ascribed to the evolution of water in hydrous zirconia and the decomposition of $KHCO_3$. This was confirmed by an increase in the ionic currents of $m/z = 18(H_2O^+)$ and 44 $(CO_2{}^+)$ with maxima at around 135 and 228 °C. A sharp exothermic effect at about 516 °C was observed without weight loss for the crystallization of amorphous ZrO_2. The exothermic effect for the crystallization of pure ZrO_2 is at about 410 °C in DTA curve [7]. Thus, the introduction of potassium ions in ZrO_2 shifts the crystallization temperature of ZrO_2 to higher temperatures. The sulfation of zirconia has the same effect [7]. In the measurement of KHC-ZRO, two endothermic effects and corresponding DTG peaks at around 133 and 159 °C clearly indicate the decomposition of $KHCO_3$ on ZrO_2 with about 3% weight loss between 100 and 200 °C, which is different from that of KHC-ZRH. The carbon contents of KHC-ZRH and KHC-ZRO after thermal analysis up to 700 °C were 0.33 and 0.63% respectively, which corresponds with the elemental analysis of these samples after calcination at 600 °C (0.46 and 0.72%, respectively, in table 1). These results indicate that the loaded potassium compounds do not completely decompose; this is also reported by Wang *et al.* for KNO_3/ZrO_2. For a sample with 20% KNO_3 on ZrO_2, the percentage of decomposed KNO_3 was only 7.6 [25]. This, and our results, could be explained by the formation of layers of thermally stable potassium compounds on the zirconia surface.

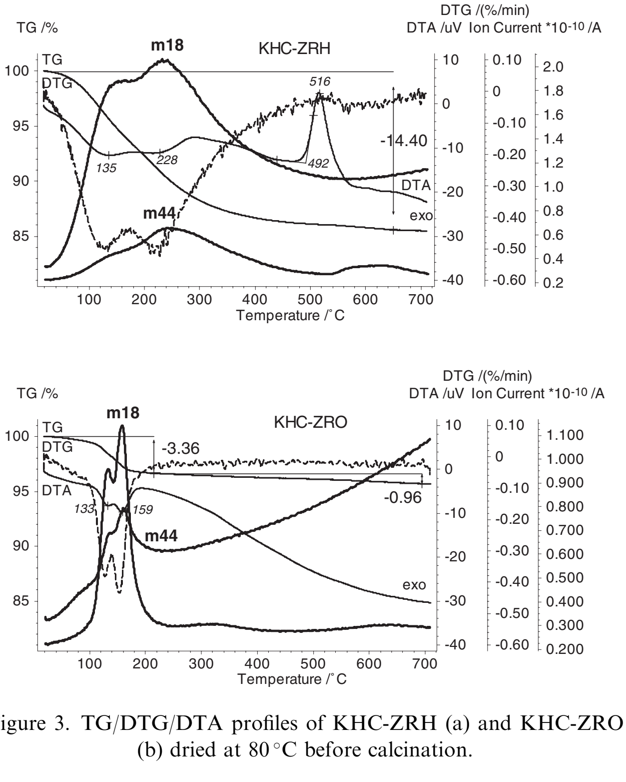


Figure 3. TG/DTG/DTA profiles of KHC-ZRH (a) and KHC-ZRO (b) dried at 80 °C before calcination.

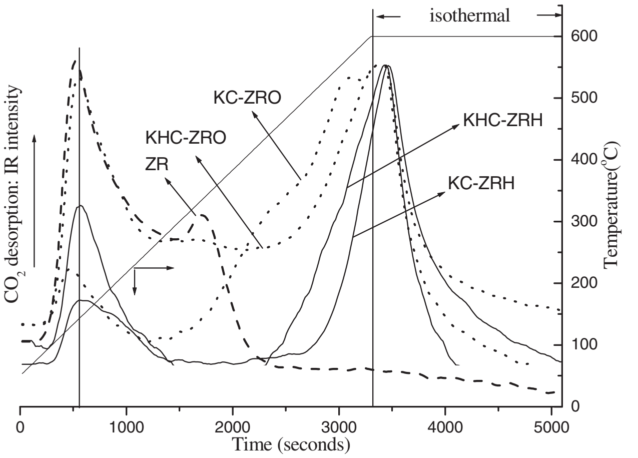


Figure 4. Temperature-programmed desorption of CO_2.

The CO_2-TPD results (figure 4) show that pure ZrO_2 has basic sites indicated by two desorption maxima at about 135 and 335 °C. The potassium-modified zirconia samples, like ZrO_2, show an initial desorption maximum at around 140 °C. A second step of CO_2 desorption at higher temperatures starts at around 400 °C for KC-ZRH and KHC-ZRH, but at a lower temperature, 250 instead of 400 °C, for the ZRO samples. This increase in the CO_2 profile intensity continues up to 600 °C and lasts for 5–10 min under isothermal conditions. These results suggest that modified anhydrous zirconia (ZRO samples) has a wider distribution of basic sites than modified hydrous zirconia (ZRH samples). The second step of desorption of the modified samples indicates their stronger basic sites in comparison to those of ZrO_2.

CO_2 desorption at higher temperatures could be attributed to strong basic sites formed by K_2O extrafine particles on the surfaces of ZrO_2 during decomposition. This has been reported by Zhu *et al.* [19]. He also excluded the possibility of some unusual oxides of potassium as the main basic sites on KNO_3/Al_2O_3. Hathaway *et al.* [16,17] and Kim *et al.*[18] also suggested in the case of Cs-modified zeolites that the decomposition product, cesium oxide, forms the active sites.

Both acid and base catalysts can catalyze the double-bond isomerization of 1-butene. Generally, the cis/trans ratio of 2-butene produced by isomerization of 1-butene is higher for base-catalyzed reactions [18,24]. The results of the double-bond isomerization of 1-butene are given in table 2 with the normalized yields of 2-butene at 30 min for the catalysts. *Cis*/*trans*-2-butene are the exclusive products found at 150 °C (100% product

Table 2
The results of double-bond isomerization of 1-butene at 150 °C

Catalyst	Weight (mg)	Yield of 2-butene (%)				Yield/mass (%/mg) at 30 min	Average cis/trans ratios
		10 min	30 min	60 min	90 min		
ZR	330	24.1	21.7	19.1	16.7	0.066	4.0
KC-ZRH	395	69.7	54.2	42.4	35.2	0.137	5.3
KC-ZRH[a]	395	75.2	62.9	49.6	40.7	0.159	5.1
KHC-ZRH	361	62.7	44.3	30.2	22.8	0.123	5.3
KAC-ZRH	411	74.1	63.8	52.1	44.7	0.155	5.0
KAC-ZRH[a]	411	63.2	58.5	50.2	44.8	0.142	5.2
KN-ZRH	379	9.1	6.8	5.6	4.7	0.018	3.9
KC-ZRO	380	51.9	40.8	30.8	25.1	0.107	5.1
KHC-ZRO	350	53.1	36.8	25.9	21.0	0.105	5.3
KAC-ZRO	316	56.5	41.3	29.6	23.4	0.131	5.0
KN-ZRO	329	4.1	3.6	2.7	2.1	0.011	2.5

[a] Second run (the same reaction procedure was repeated again).

selectivity); skeletal isomerization or alkylation did not occur. Unmodified ZrO_2, which was inactive at 60 °C in [28], had a low catalytic activity at 150 °C. About 21% yield of 2-butene with a cis/trans ratio of 3.9 was obtained after 30 min. The potassium modification of ZrO_2 resulted in an increase in the yield of 2-butene, i.e., from 21.7 up to (at the most) 63.8% after 30 min, except for the KNO_3-modified samples (table 2). The improved activity is indicated by (1) the yield/mass ratio at 30 min of 0.066 (pure zirconia) and 0.10–0.16 (potassium-modified ZrO_2) and (2) the higher cis/trans ratios (more than 5.0). This can be explained by the stronger basic sites on catalysts produced by modification and confirmed with CO_2-TPD (figure 4). According to the literature [23,24], strong active basic sites are essential for the catalysis of 1-butene isomerization. Why the KNO_3-modified samples give yields of 2-butene lower than that of ZrO_2 and lower cis/trans ratios is not clear. The catalysts prepared from the modification of hydrous zirconia are slightly more active than the corresponding catalysts from anhydrous zirconia; this could be a result of the difference in the distribution of basic sites indicated by CO_2-TPD. At the same time, the locations of the basic sites on the surface of the different zirconia (tetragonal or monoclinic) may also affect the reaction. The catalysts, KC-ZRH and KAC-ZRH, were reused without much decrease in conversion after treatment at 600 °C (table 2).

The liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone used for the catalytic experiments (scheme 1) is an important reaction for the synthesis of steroid pharmaceutical products.

Pure ZrO_2 was catalytically inactive in this reaction, but the modification of ZrO_2 with potassium salts was successful in producing catalytic activity. Thus, the target product, 2-(γ-oxobutyl)-2-methylcyclohexane-1,3-dione, was formed selectively on the catalysts, KC-ZRH, KHC-ZRH, and KAC-ZRH, within 24 h in yields of more than 95% (table 3). In contrast, KN-ZRH and KN-ZRO gave yields of only 72 and 55% respectively (not given in table 3). The rate of product formation was highest on KC-ZRO, KHC-ZRO, and KAC-ZRO. Yields of about 80–90% were achieved within 6 h.

Leaching tests performed by filtration of the catalyst from the reaction mixture after 4 or 14 h show that the

Table 3
The results of Michael addition (scheme 1) and leaching tests at room temperature

Catalyst	Yield of 2-(γ-oxobutyl)-2-methylcyclohexane-1,3-dione (%)[a]							
	2h	4h	6h	8h	24h	Leaching test		
						Before separation	After separation of the catalyst	
KC-ZRH	17	24	–	48	99	73 (14h)	95 (12h)	95(24h)
KHC-ZRH	18	32	–	56	98	82 (14h)	96 (12h)	96 (24h)
KAC-ZRH	16	30	41	52	96	–	–	–
KC-ZRO	39	63	82	93	89	66 (4h)	88 (16h)	85(24h)
KHC-ZRO	59	79	90	86	86	75 (4h)	89 (16h)	89(24h)
KAC-ZRO	36	62	81	92	96	–	–	–

[a] Related to 2-methylcyclohexane-1,3-dione.

reaction continues after removal of the solid potassium-modified zirconia catalyst. The presence of potassium ions in solution was checked and confirmed by ICP-OES. It can be concluded that potassium compounds leach from the catalyst surface into the methanolic reaction mixture. This leaching and consequent homogeneous catalysis may be explained by the weak interaction of the potassium compounds with ZrO_2 and the solubility of potassium compounds in methanol. Consequently, exclusive heterogeneous catalysis can be ruled out for the liquid-phase reaction investigated on potassium-modified zirconia in methanol. However, the catalytic results differ from those obtained for the soluble base catalyst, KOH. When KOH is used, low product yield (40%) and a mixture of various products are found. This indicates that different K species are present in the methanol solution, and that the reaction may not be a straightforward example of homogeneous catalysis.

These results show that this catalyst system is less suitable for liquid-phase reactions, although the potassium-modified ZrO_2 samples do produce both higher selectivities and higher yields than KOH, and catalysts with potassium or alkali metal cations have been used successfully in vapor-phase reactions. The nature of the interaction between the support, ZrO_2 or Al_2O_3, with potassium or other alkali metal cations is open to further discussion [31].

4. Summary and Conclusions

In summary, the properties and the activities of the catalysts can be influenced by a variety of parameters, such as the zirconia precursor and the potassium modifying agent. High product yields and selectivities were also obtained for the liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone in methanol, but leaching could not be prevented. The following can be concluded:

1. Modified hydrous zirconia forms the metastable, tetragonal ZrO_2 phase after calcination; the phase of modified anhydrous zirconia, on the other hand, is monoclinic. The specific surface areas of the modified samples are much lower than that of ZrO_2. The potassium compounds on hydrous zirconia decompose in a broader temperature range than those on anhydrous zirconia.
2. Stronger basic sites are produced after modification, and modified anhydrous zirconia has a wider distribution of basic site strengths than modified hydrous zirconia.
3. Potassium-modified zirconia, except for that modified with KNO_3, give higher yields and cis/trans ratios of 2-butene in the double-bond isomerization of 1-butene and is reusable.
4. Potassium-modified zirconia is less suitable as a solid-base catalyst for liquid-phase reactions in methanol because of potassium leaching effects.

Acknowledgments

We acknowledge the Bundesministerium für Bildung und Forschung (BMBF) for their financial support. We would also like to thank Elfriede Lieske for the catalytic work, Sigrid Bäßler for the TPD measurements, and Dr. Michael Feist for the TG-DTG-DTA measurements.

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